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# **Synthesis and Characterization of Chlorinated Bisphenol-Based Polymers and Polycarbodiimides as Inherently Fire-Safe Polymers**

August 2000

Final Report

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## EXECUTIVE SUMMARY

Two different types of polymers were synthesized and their degradation and combustion behavior were investigated. The first class, 1,1-dichloro-2,2-(4-hydroxyphenyl)ethylidene (bisphenol C) based polymers, were found to be among the most fire-resistant polymers with peak heat release capacities as low as 20 J/g-K. Polymers containing bisphenol C all exhibited exothermic decomposition behavior. When compared to corresponding bisphenol-A-based polymers, these bisphenol-C-containing polymers had higher char yields and lower decomposition temperatures. The presence of bisphenol C in materials, whether as a co-monomer or blends, showed a char enhancement effect; yielding higher char than what is expected by a purely additive effect.

Bisphenol C polyarylates and polycarbonates yielded large amounts of HCl and carbon dioxide upon decomposition. Compared with other bisphenol-based polymers, polycarbonates and polyarylates containing bisphenol C yielded significantly less amounts of monomer. Decreasing the concentration of bisphenol C in the copolymers or blends yielded relatively more monomer in the degradation products.

The second class of polymers studied were polycarbodiimides, which generally decompose in an endothermic manner to yield quantitative amounts of monomer. The incorporation of TEMPO-containing side-chain substituents altered the degradation. TEMPO-based polycarbodiimides decomposed in an exothermic fashion and yielded several other degradation products in addition to the original monomer. These free-radical-containing polymers showed a 25 % reduction in the peak heat release capacity

when compared with the control polymer. Neither polymer was found to be fire resistant which is due to their high organic content and essentially 100 % weight loss during decomposition.

## CHAPTER 1

### POLYMER FLAMMABILITY

#### 1.1 Introduction

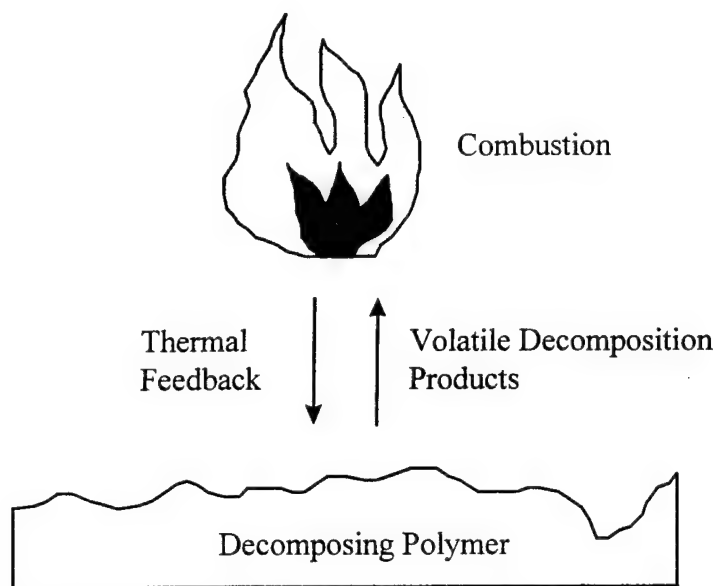
Organic polymers have found increasing use in more demanding applications due to their low density, high specific properties such as strength-to-density ratios, ease of fabrication and other properties not found in metal and ceramic materials.<sup>1</sup> The use of polymers in electrical, transportation and building applications requires the use of flame-retarded polymers.<sup>2</sup> There are many more potential applications which have eluded the use of polymers because of generally inherent flammability of polymers.<sup>3</sup> The loss of life and property are the main factors driving the research on flammability and fire retardancy of polymers. Annually in the United States, fire accounts for more than 6,000 deaths and \$10 billion in property damage.<sup>4</sup> New requirements legislated by governments will greatly affect the use of polymers, especially in building and transportation applications.<sup>5</sup> Such mandates include eliminating environmentally unfriendly halogen-containing flame-retardant materials and high-heat-release materials (i.e., highly flammable materials).

It was recognized a long time ago that certain compounds could be added to natural polymers (wood, wool, cotton) to inhibit their ignition.<sup>6</sup> Today, this same approach is used for many commodity polymers. Even though these materials have been made to resist ignition, this occurs only for fires with small heat fluxes. The search for new non-flammable materials focuses on many areas, but a few are at the forefront of

research. These include thermally stable, low-heat-release organic polymers, inorganic polymers, and new nonhalogen-containing polymers and flame retardants. Although many promising materials have been found with respect to fire-retardant properties, use has been limited by a number of factors, including cost, environmental stability, difficulty of processing and toxicity of decomposition products.

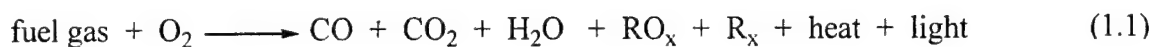
## **1.2 Combustion of Polymers**

There are three components needed to sustain combustion: fuel, an oxidizer and heat.<sup>2</sup> In a very basic explanation the burning process for a polymer can be broken into three major steps: heating, degradation and combustion.<sup>3</sup> The first step is the heating of the polymer to a temperature at which degradation occurs to liberate volatile small molecule products. Since combustion generally occurs in the vapor phase, the polymer must decompose to combustible gases. If there is an ignition source or the temperature is hot enough and the degradation products are combustible then flaming combustion will occur. This combustion reaction generates heat which can contribute to further polymer decomposition and thus continuous self-sustained combustion occurs. Figure 1.1 shows a schematic of the combustion cycle. The combustion process depends on such variables as heat release (energy from the combustion reaction), heat release rate (how fast the energy is liberated) and rate of decomposition (the rate at which the polymer potentially fuels the combustion reaction). A more detailed description of how these variables affect the combustion properties are given in Chapter 3.



**Figure 1.1** Schematic of combustion cycle.

In the atmosphere the oxygen acts as the oxidizer for the organic fuel from the decomposing polymer. The overall combustion reaction can be represented by the following reaction.<sup>5</sup>



If complete combustion were to occur, water and carbon dioxide would be the only products from a hydrocarbon polymer. This is usually not the case. Products of incomplete combustion as shown in Eq. 1.1 include carbon monoxide and other hydrocarbon molecules ( $\text{RO}_x$  and  $\text{R}_x$ ). Combustion reactions are known to proceed through a series of radical reactions.<sup>7</sup> Inhibition of combustion can be obtained by having polymers that do not decompose or decompose to yield non-flammable gases. Flame

retardants can also break the combustion cycle by consuming highly reactive  $H\cdot$  and  $HO\cdot$  species in the vapor phase.<sup>8</sup>

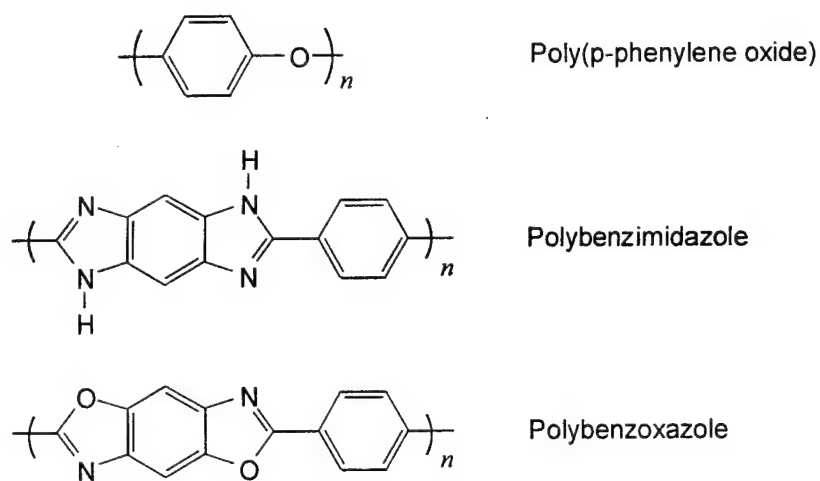
### **1.3 Strategies For Reducing Polymer Flammability**

As stated in the previous section, there are essentially three components needed to sustain combustion. Removal of any one component from the burning cycle will inhibit or shut down the combustion cycle. The variables that can be controlled for most applications affect the generation of volatile decomposition products and their contribution through heat radiating back to the decomposing polymer.

Methods for reducing the flammability of polymers can be grouped into two categories: inherently nonflammable polymers and flame-retardant additives and modifiers. Any organic polymer will burn when subjected to enough heat and/or oxygen. Therefore the problem becomes designing polymers that delay the time to combustion, decrease the rate of decomposition and decrease the energy of the combustion reaction. Using polymers that do not decompose to give off any fuel is the most straightforward route to reducing the contribution of the polymer to a fire. This can also be the most difficult. Whereas synthesizing such a material may be possible, the problem lies in having a material with the combination of desired properties, processability and cost. Other routes include polymers that decompose but yield reduced amount of gases or noncombustible gases to reduce or remove the exothermic gas phase reaction that promotes further polymer decomposition (i.e. liberate large amounts of water or other noncombustible gases).



Nonflammable polymers include thermally stable materials and inorganic polymers. Thermally stable polymers are characterized by their high aromatic contents, high decomposition temperatures and high char yields. Polymers of this type include polyphenylene oxides, polybenzimidazoles and polybenzoxazoles (Figure 1.2). These polymers have been limited in use mainly due to the difficult and costly processing required by these generally infusible materials. Most of these polymers are typically only soluble in very strong acids and show no  $T_g$  or melting behavior prior to decomposition, which also limits processing to only fiber and perhaps film.



**Figure 1.2** Some examples of thermally stable polymers.

Flame retardants have been the most widely used method for reducing the flammability of polymers. Lower cost and ease of use have driven the use of small-molecule additive-type flame retardants, which are physically mixed with the polymer. This method has the drawback of affecting the mechanical properties of the polymer. It has also been found that the effectiveness of these flame retardants is reduced over time

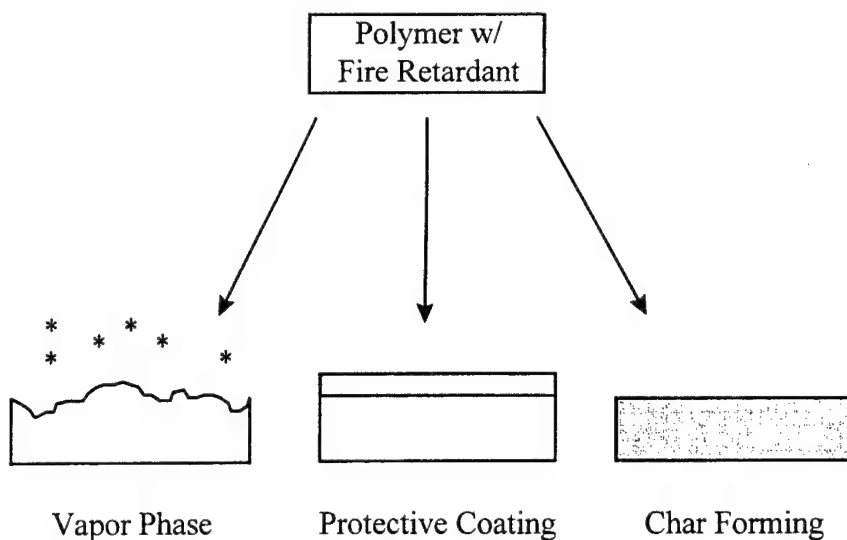
from their being leached out of the system due to diffusion and volatilization. There is also concern over the post-consumer environmental effects whether they are incinerated or land filled. The problem thus lies in making a polymer flame retardant while maintaining low cost, environmental friendliness and mechanical properties.

To overcome some of these deficiencies, reactive-type flame retardants have been developed. This generally includes modifying a monomer to include halogens, phosphorus or other flame retardant elements. These flame-retardant monomers can be polymerized to give a homopolymer or polymerized with the unmodified monomer to give copolymers. Reactive-type flame retardants are more expensive than additive-type because they generally require the development of a new monomer, polymerization reaction and processing.

#### **1.4 Flame-Retardant Mechanisms**

Flame retardants can be designed to act by one or a combination of chemical and physical interactions in either the vapor or condensed phase.<sup>9</sup> The mechanism by which a particular flame retardant works depends on the chemical composition of the flame retardant as well as the polymer into which it is incorporated. A very general schematic of possible routes to flame retardant action is shown in Figure 1.3. Mechanisms by which flame retardants function include: inert gas dilution, thermal quenching, protective coatings, physical dilution, chemical interaction.<sup>10</sup> Many flame retardants have been found that act through a combination of different mechanisms.

The combustion process can be retarded through a physical action by cooling, formation of a protective layer or dilution. Inert gas dilution works by liberating large



**Figure 1.3** Schematic of fire retardant strategies.

amounts of noncombustible gases that reduce the fuel concentration below that which is needed to sustain combustion. The endothermic decomposition of a flame retardant, if large enough, can reduce the heat to below the limit required to sustain combustion.

Also, a flame retardant can react with itself or with the decomposing polymer to form a protective layer which can act as a thermal insulator as well as a barrier to the mixing of oxygen and fuel gases. Inert fillers reduce the potential amount of combustible fuel in addition to acting as a heat sink.

Flame retardants that work by a chemical means are generally more efficient than ones that work by a physical action.<sup>2</sup> In the vapor phase, the flame retardant and/or its decomposition products can inhibit the combustion reactions by acting as radical traps. In the condensed phase, the flame retardant reacts with the polymer substrate to form a

crosslinked network of carbonaceous char which reduces the amount of combustible gas given off.

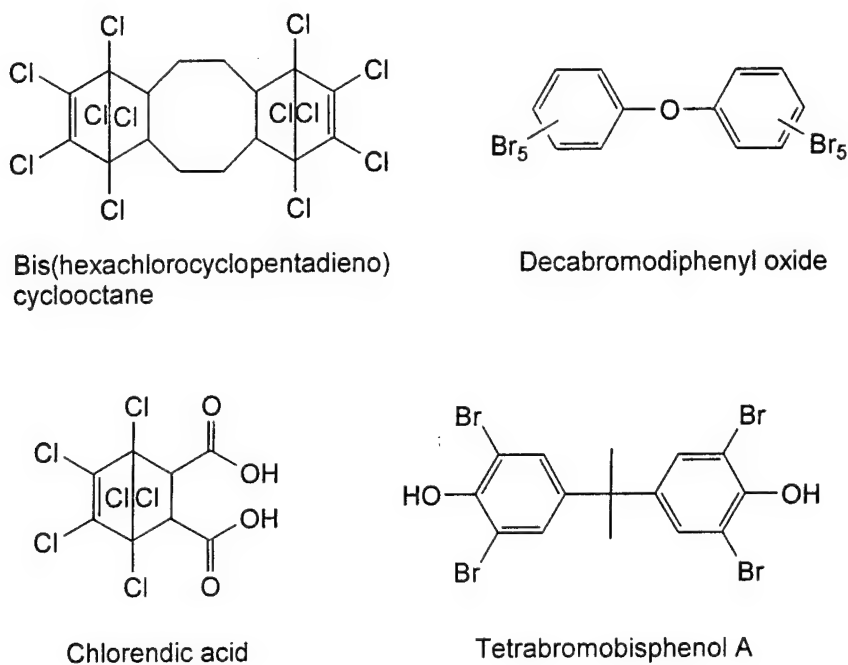
## **1.5 Flame Retardants**

Flame-retardant compounds are characterized as containing certain elements. These elements include antimony, aluminum, phosphorus, boron, halogens (bromine and chlorine), silicon and nitrogen. Many of these compounds have synergistic effects with one or more of the other compounds, and a few even have antagonistic effects with each other. In the following section, a brief description of a few of the more important flame retardants is given.

### **1.5.1 Halogenated Flame Retardants**

Organohalogens are proposed to act in the vapor phase as radical scavengers by reaction with  $H\cdot$  and  $HO\cdot$  species. Iodine is the most effective halogen, followed by bromine and then chlorine. Iodine-containing compounds are not commercially used as flame retardants due to the weak iodine-carbon bond. Fluorine-containing compounds are expensive and generally ineffective due to the strength of the carbon-fluorine bond. Bromine is twice as efficient as chlorine on a weight basis and four times as efficient on a molar basis.<sup>11</sup> The thermal stability of the flame retardant compounds increases as brominated aliphatic < chlorinated aliphatic < brominated aromatic. Although there is increasing legislation against the manufacture and use of halogenated compounds, they are still used for many applications due to their high efficiency. By-products of the decomposition of halogenated flame retardants can be corrosive and contain toxic hydrogen halides. Halogenated compounds have been used as both additive- and

reactive-type flame-retardants.<sup>7,10</sup> Examples of a few of the most common halogenated flame retardants are shown in Figure 1.4. Common requirements in order to obtain polymers that are considered self-extinguishing range from 5-20 % for bromine and 10-40 % for chlorine. When antimony oxide is used as a synergist, the levels are reduced two to three times.

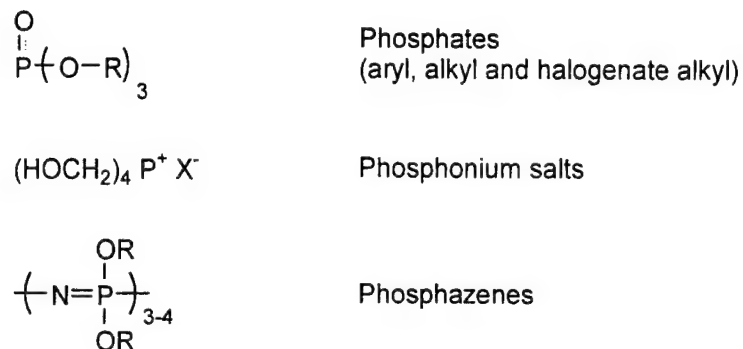


**Figure 1.4** Examples of halogenated flame retardants.

### 1.5.2 Phosphorus-Based Flame Retardants

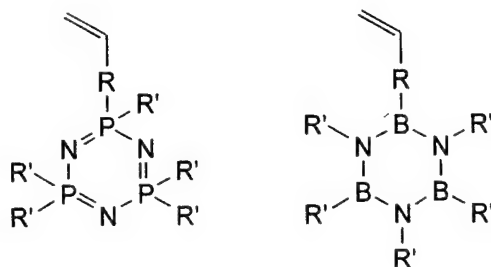
Phosphorus-containing compounds have been found to impart flame retardancy, especially in combination with nitrogen and organohalogens. Phosphorus flame retardants can be additive or reactive types.<sup>12,13</sup> They have been known to act in both the vapor and condensed phase depending on the compound. In the vapor phase they act as

radical scavengers, and in the condensed phase they increase the char yield. Flame retardants based on phosphorus compounds can be elemental, inorganic or organic. Commonly used phosphorus flame retardants include alkyl and aryl phosphates, phosphonium salts and phosphazenes (Figure 1.5).



**Figure 1.5** Examples of phosphorus-based flame retardants.

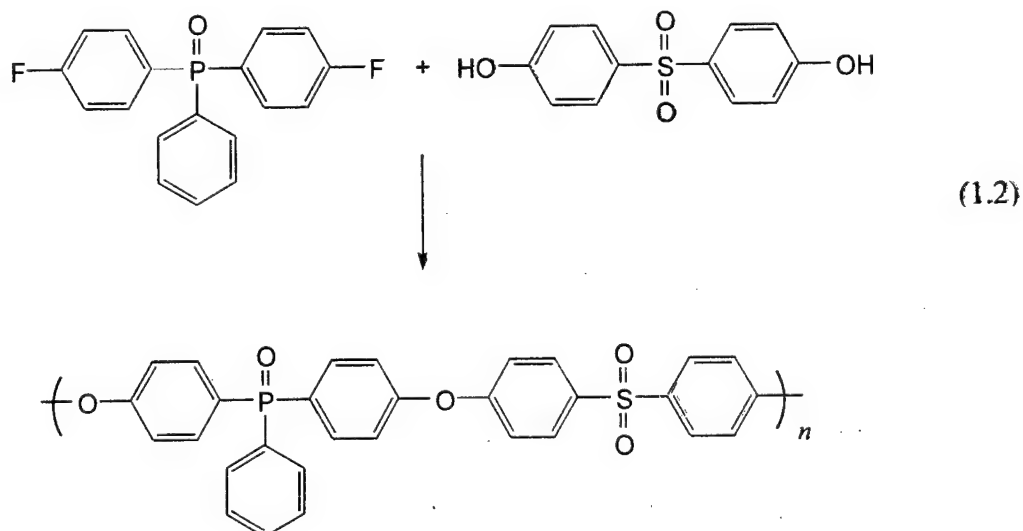
The use of phosphazenes as flame retardants for cellulose has been known for some time. Allen has prepared phosphazene vinyl monomers by modifying phosphazenes to contain olefinic substituents.<sup>14</sup> He found that a few mole percent of the phosphazene monomer copolymerized with styrene yielded materials which do not burn or produce smoke in laboratory experiments. A generic structure for functionalized phosphazenes is shown in Figure 1.6 where R can be an ether, acrylate or styrenic linkage and R' can be fluorine, an alkoxide or a phenoxide. A pentafluorophosphazene ring attached to the polymer backbone imparted flame-retardant properties when copolymerized with styrene or vinylbenzyl chloride.<sup>15</sup> Flammability was tested qualitatively by a match test and found to self-extinguish when the flame was removed.



**Figure 1.6** Structure of phosphazene and borazine rings attached to reactive monomers.

Inoue prepared similar polymers and found a large increase in the char yield and self-extinguishing properties.<sup>16</sup>

McGrath and co-workers found that aryl phosphine oxides are effective reactive-type flame retardants.<sup>17-19</sup> These phosphorus-containing monomers are hydrolytically stable and easily incorporated into several engineering thermoplastics by a nucleophilic-aromatic-substitution polycondensation route (Eq. 1.2). Poly(arylene ether sulfone)s containing the aryl phosphine oxide had improved thermal stability in air and increased char yield when compared with a control poly(aryl ether sulfone). Peak heat release rate



measured by cone calorimetry was reduced from 170 kW/m<sup>2</sup> for Amoco Udel (a polyarylethersulfone) to 85 +/- 40 kW/m<sup>2</sup> for a polysulfone containing the phosphorus monomer (5.9 wt% P). While peak heat release rates are decreased and the char yields are increased for these phosphine-containing systems, the amount of carbon monoxide produced is also increased.<sup>20</sup> This was observed for nylon-6,6 containing triarylphosphine oxide. The amount of carbon monoxide produced increased with increasing amounts of the incorporated phosphine oxide. The addition of 80 % of triarylphosphine oxide increased the amount of carbon monoxide 6-fold. Other systems that the triarylphosphine oxide has been incorporated into, include poly(arylene ether ketone)s, polyimides, polybenzoxazoles, polycarbonates,<sup>21</sup> polyesters<sup>21</sup> and polyamides.<sup>20</sup>

### 1.5.3 Nitrogen-Based Flame Retardants

Nitrogen compounds make up a very small percentage of flame retardants in commercial use but are becoming more widely used because of concerns over toxic halogenated decomposition byproducts.<sup>22</sup> Nitrogen-based flame retardants include melamine, melamine cyanurate, melamine salts and guanidines.<sup>1,8</sup> These are generally used with nitrogen-based polymers, and therefore, do not add any new elements to the polymer. Melamine added to a polyurethane foam decreased the peak heat release rate when measured by cone calorimetry.<sup>23</sup> The advantages of nitrogen compounds include low toxicity, absence of corrosive combustion products, and low smoke evolution. However, some nitrogen compounds have been known to give off hydrogen cyanide as a combustion product, which is more toxic than hydrogen halides. The efficiency of



nitrogen flame retardants lies somewhere between that of halogenated flame retardants and that of aluminum trihydrate and antimony oxide. They are thought to act in the condensed phase as well as by diluting combustion gases. For nitrogen-containing systems, the presence of nitrogen does not necessarily make for a more fire-resistant material. For example when comparing polyurethanes with polyamides (Nomex™), the polyurethane can be extremely flammable while the aromatic polyamide is thermally stable and generally considered fire resistant.

#### **1.5.4 Silicon-Containing Flame Retardants**

Little research has been done on the effectiveness of silicon compounds as flame retardants. One study by Kambour at General Electric found that polycarbonates containing siloxane rings exhibited high levels of char.<sup>24</sup> Block copolymers of polydimethylsiloxane with bisphenol A polycarbonate exhibited synergistic effects when measured by limiting oxygen index (LOI). The largest LOI value of near 50 was obtained with 8-12 wt% dimethylsiloxane (LOI = 25 for bisphenol A polycarbonate and LOI = 22 for dimethylsiloxane). Synergistic effects were found with bisphenol fluorene, bisphenol chloral and phenolphthalein polycarbonate and polystyrene. For bisphenol A polycarbonate, the synergism found in limiting oxygen index correlates with an increase amount of char and an increase in the oxidative stability of char.

One other study by researchers at Dow Corning found that powders of polydimethylsiloxane and fumed silica modified to contain organofunctional groups showed decreases in peak heat release rate, peak carbon monoxide evolution and smoke generation.<sup>25</sup> Effects were found for polycarbonate, polypropylene and polyphenylene

oxide although, in order for polymer systems with silicone additives to pass UL-94 and LOI tests, they need to be combined with other flame-retardant additives.

#### **1.5.5 Boron-Based Flame Retardants**

Although boron-based compounds are some of the oldest flame retardants, they have been less studied due to their cost. Boron has been proposed to act both in the condensed phase and the vapor phase. Most commercial boron-based flame retardants are inorganic although limited research has been done on organoboron compounds such as borazines. These compounds have high thermal stability and can be modified to contain reactive organic groups (Figure 1.6). For borazines, the vinyl group can be directly linked to the inorganic ring or R can be styrenic. Borazines can be substituted with olefinic groups in a similar manner to phosphazenes. Vinyl borazines have been copolymerized with styrene although combustion properties have not been measured. Heating of many vinylborazine polymers yields ceramic materials of boron nitride.<sup>26</sup>

#### **1.5.6 Inorganic Flame Retardants**

There are many inorganic compounds that have been found to impart some degree of flame retardancy to polymers.<sup>27,28</sup> The two most commonly used inorganic flame retardants are antimony oxides ( $\text{Sb}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_5$ ) and alumina trihydrate ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ). Antimony oxides are rarely used alone but have found wide spread use as synergist for halogen-containing flame retardants. Addition of antimony oxides generally allows for a significant reduction in the total amount of flame retardants needed to impart fire-retardant characteristics. They function by forming antimony halides and oxyhalides with hydrogen halides and organic halogens from the decomposition of the flame retardants.

They are proposed to be gas-phase flame retardants but have also been shown to have effects on the condensed-phase reactions.

Alumina trihydrate is the most widely used flame retardant. It can only be used with polymers that are processed at low temperatures. It functions in both the gas phase and condensed phase. Alumina trihydrate acts by liberating water at around 250 °C through an endothermic process. The total amount of combustible gases is reduced by dilution and the large heat capacity of water acts as a thermal sink.

### **1.6 Polymeric Flame Retardants**

While flame retardants discussed in the previous section were based on key chemical elements, generally these were discussed in reference to their possible mechanisms and in cases of known additive- and reactive-type flame retardants. In the prior section, reactive-type flame retardants were discussed but in reference to the fact that they were only designed to help the flame retardancy of the polymer into which they were incorporated. Here, examples of a few cases where polymers have been designed to be additive-type flame retardants are discussed.

Polymeric flame retardants have been much less studied than their small molecule counterparts, probably due to the potential for phase separation that occurs in many polymer blends. Physical and mechanical properties of the polymer substrate, for better or for worse, are generally less affected by the incorporation of a polymeric flame retardant. Also, the polymeric flame retardant should decompose below or at the same temperature as the polymer substrate. Polymeric flame retardants remove the problem of leaching from the system with time.

One such system is using polydibromostyrene as a flame retardant.<sup>29</sup> In the past, brominated polystyrenes were prepared by bromination of polystyrene which can lead to labile aliphatic and benzylic bromine on the polymer backbone. Polydibromostyrene contains only aromatic bromine and therefore is more thermally stable. While similar loadings compared with similar brominated small-molecule flame retardants were needed to impart the necessary flame retardance, the brominated polystyrene had better thermal stability and less of an effect on the final material properties. The thermal stability is required for blending with such polymers as nylons and polyesters (polybutylene terephthalate, PBT) that must be processed at high temperatures.

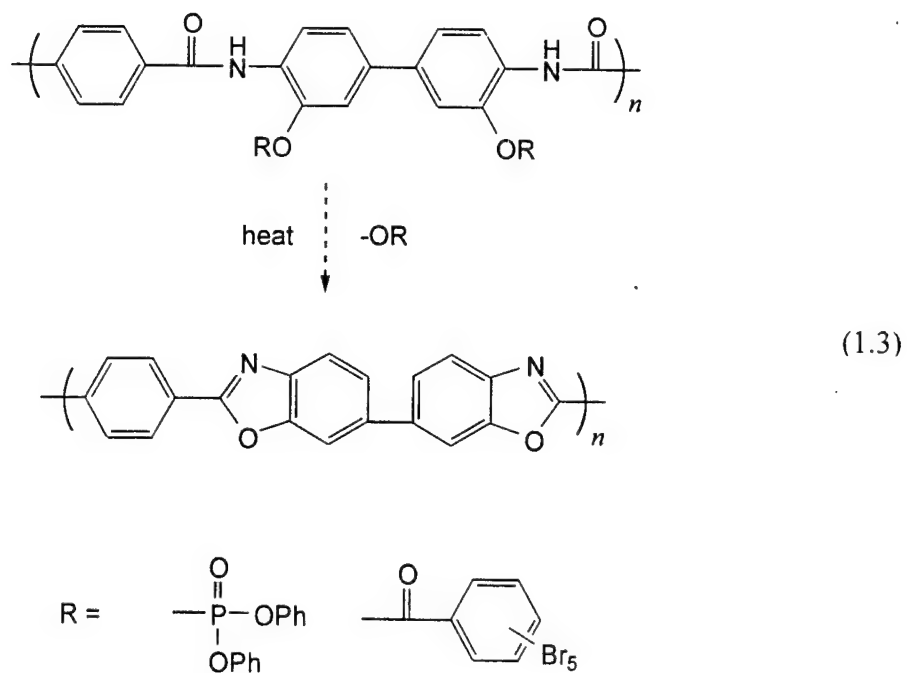
Polyphosphazenes are among some of the most fire-resistant polymers. Oligomeric phosphazenes (Figure 1.5) have been used for additive-type flame retardants for natural fibers and phosphazenes have been proposed as reactive-type flame retardants. Polyphosphazenes can find potential uses as polymeric flame retardants for blends and interpenetrating networks (IPNs).<sup>30</sup> The alternating phosphorus nitrogen backbone is inherently thermally and oxidatively stable. There are more than 700 different polyphosphazenes that have been reported that differ in the type of organic side group they possess.<sup>31,32</sup> Thus far, polyphosphazenes have been limited to military applications due to their high cost of production. New routes to polyphosphazenes are being investigated as well as the effect of polyphosphazenes on the decomposition and combustion behavior of conventional organic polymers (i.e. polyurethanes).

## 1.7 Thermally Stable, Flame Retardant Polymers

As mentioned previously, the most straightforward method for preparing fire-retardant polymeric materials is to make inherently fire-retardant polymers. Some new perspectives on making fire-retardant polymers while trying to maintain good processability have been under recent investigation.

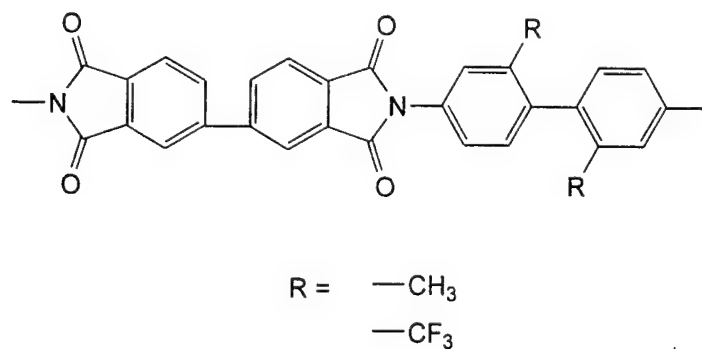
Polybenzoxazoles (Figure 1.2) and polyimides are both thermally stable and have good flammability properties but are difficult to process due to infusibility and limited solubility. These polymers are prepared by cyclization of precursor polymers, polyhydroxyamides and polyamic acids. Research has begun on the investigation of using precursor materials which at high temperatures will cyclize to give the thermally stable polymers.<sup>33-35</sup> The precursor polymers liberate water upon cyclization but can be modified with a number of phosphorus and brominated functionalities, to give off flame-retardants (Eq 1.3). Thermal and mechanical properties of phosphorus substituted polyamic acids have been studied.<sup>36</sup> These phosphorylated precursor materials were prepared directly from polyamic acid, PMDA-ODA, (pyromellitic dianhydride-4,4'-oxydianiline). Thin films of these polymers that had been partially imidized were found to have a high Limiting Oxygen Index (LOI), 67-78, and high char yields, 54-63 % at 850 °C.

As described above, polyimides are usually prepared from the precursor polymer, polyamic acid. The precursor polymer allows for the fabrication of films and coatings from solution followed by removal of solvent and thermal cyclization. Other modifications to polyimides include using a substituted aromatic biphenyl in order to break up the crystallinity and provide polymers that will swell in a solvent

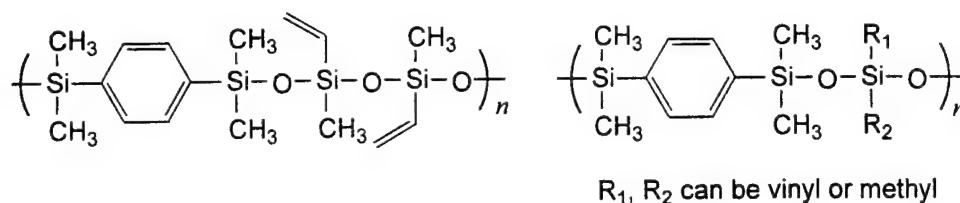


(Figure 1.7).<sup>37-40</sup> These polyimides can be spun into fibers by dry-jet-wet spinning from m-cresol.

Silphenylene siloxane elastomers have both low-temperature flexibility and high-temperature stability. The incorporation of vinyl group substituents (Figure 1.8) allows for high char yields. The preparation of these materials and their stability has been



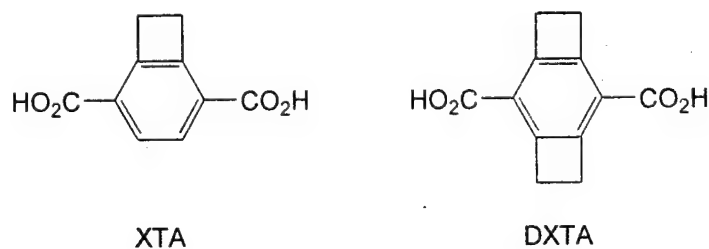
**Figure 1.7** Gel-spinnable polyimides.



**Figure 1.8** Examples of silphenylene siloxane polymers.

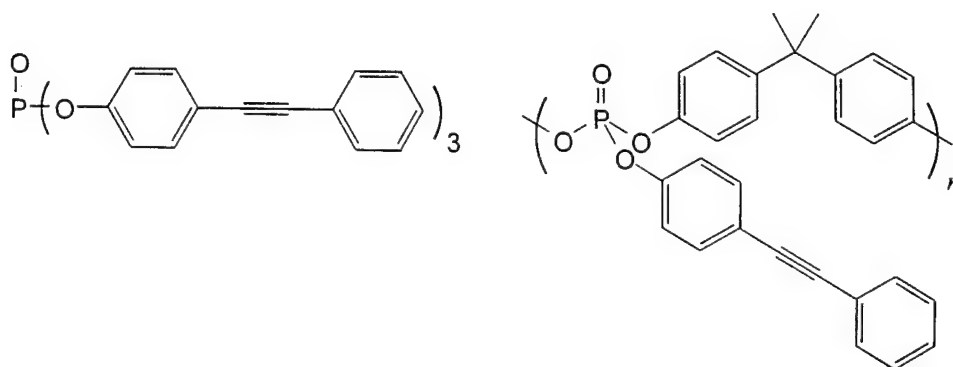
investigated.<sup>41,42</sup> These vinyl-containing polymers show a large exotherm in the 300-400 °C range indicating the presence of a crosslinking reaction. The polymers also show increasing char yields with increasing vinyl content. These vinyl containing materials have low Tg's both in uncrosslinked and crosslinked forms.

Another polymer that has been investigated uses a benzocyclobutene (BCB) functionalized variant of terephthalic acid (XTA) (Figure 1.9).<sup>43,44</sup> Research on incorporating these monomers into polyesters and copolyesters has been done to determine the effect of the BCB moiety on degradation behavior. This moiety can potentially be incorporated into polyamides, polyaryl ketones, polyurethanes and polyureas. The thermally labile BCB group is stable at processing conditions, but at higher thermal stresses (350 °C) it undergoes an exothermic crosslinking reaction without any weight loss.



**Figure 1.9** Examples of BCB-type monomers.

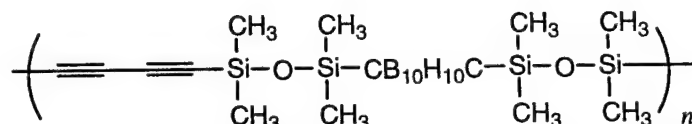
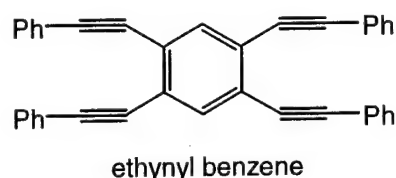
Polymers containing alkynes have been investigated as potential fire retardants. Alkynes have the ability to form crosslinked alkenes and cyclotrimeric crosslinks. Small-molecule flame retardants and polymers were prepared that contained both phosphorus and alkynes.<sup>45</sup> Examples are shown in Figure 1.10. It was determined that the alkyne is a better char-inducing group than phosphorus. The higher the alkyne to phosphorus ratio the greater the char yields. Depending on the compound, these materials crosslink in the temperature range of 200-450 °C. These materials were blended with polycarbonates at 10 wt% loadings to yield UL-94 V-0 ratings. (See section 3.3 for a description of ratings.)



**Figure 1.10** Examples of alkyne-containing materials.

Similarly, thermally and oxidatively stable materials are being investigated that are based on multi-ethynylbenzene and inorganic-organic hybrid polymers (Figure 1.11).<sup>46-48</sup> These materials show exceptional oxidative stability and fire resistance. The reason for incorporation of inorganic silicon and boron was to increase the oxidative stability of the carbon material that was formed upon crosslinking of the





**Figure 1.11** Inorganic-organic composites containing reactive acetylene groups.

acetylenes. These materials showed exothermic peaks in the temperature range of 200-400 °C.

## 1.8 Motivation For Current Research

Polymers account for much of the materials used in the interior of aircrafts including seating, overhead bins, acoustical insulation and carpet.<sup>49</sup> In addition to the large number of potentially combustible materials, safety problems are compounded by the inherent difficulty of a large number of people escaping from a highly confined compartment.<sup>50</sup> Secondly, the potential for a severe fire is posed by the large amount of flammable jet fuel. Flame-retardant materials have generally been designed to meet the needs of the application. For most applications, increased ignition resistance to a small flame is sufficient, and at least allows for time to escape. Here the potential for a large fire, with high heat flux, renders many of these materials useless against thermal degradation and combustion.

Approximately forty percent of the casualties in survivable commercial airline accidents are due to the effects of fire. The Federal Aviation Administration has made it

a goal to remove burning of aircraft interiors, as a cause of death.<sup>51</sup> While no organic polymer can be made completely fire resistant, polymers that delay the time to flash-over allow for more time for passengers to escape after a crash. Long-term research goals have been set to reduce the peak heat release of materials that go into aircraft interiors. A goal of zero peak heat release would allow an additional 10-15 minutes for passengers to escape, whereas the current time frame is only 2-3 minutes.

This research has focused on synthesizing fire-resistant polymers and investigating their decomposition and combustion properties. This work is described in the following chapters.

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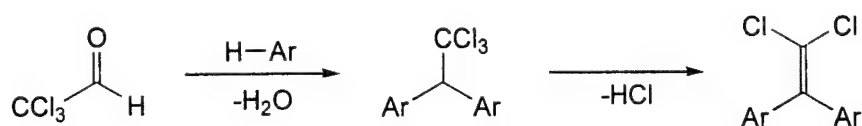
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## CHAPTER 2

### SYNTHESIS OF BISPHENOL-C-BASED MATERIALS

#### 2.1 Introduction

Compounds derived from the condensation of chloral (1,1,1-trichloroacetaldehyde) with aromatics have been known for more than 100 years. These compounds can subsequently be dehydrohalogenated to yield dichloroethylidene (DCE) type compounds. Figure 2.1 shows a generic scheme for the preparation of DCE compounds where the aromatic compound can be benzene, toluene, phenol, anisole or a halobenzene.



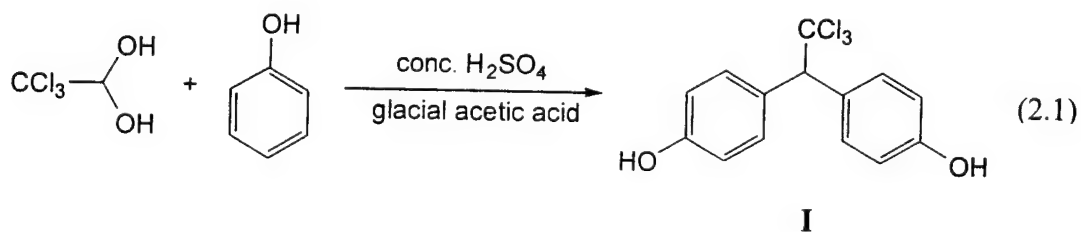
**Figure 2.1** Reaction scheme for synthesizing dichloroethylidene (DCE) containing compounds.

Compounds containing the DCE moiety have been functionalized with a number different reactive groups including alcohols,<sup>1,2</sup> amines, isocyanates,<sup>3,4</sup> acid chlorides and sulfonyl chlorides.<sup>5</sup> These monomers have been incorporated into many different polymers including polycarbonates, polyesters,<sup>6,7</sup> polyformals, polysulfones, polyethers,<sup>8</sup> polyurethanes,<sup>4,9</sup> polyureas,<sup>3</sup> polysulphonates and polyamides. A review of these materials was recently published in 1994.<sup>10</sup>

Polymers containing the DCE moiety have been reported to be self-extinguishing.<sup>3,4,11-13</sup> In this chapter, the synthesis of some of these materials and related compounds is discussed. The degradation and combustion behavior of these materials will be described in Chapter 3.

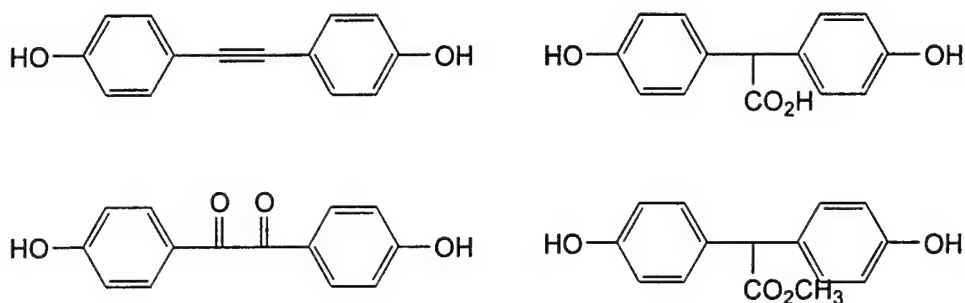
## 2.2 Bisphenol-C-Based Materials

The condensation reaction of chloral with phenol was first reported in 1874.<sup>14</sup> Other methods have been used since then, including sulfuric acid/methylene chloride,<sup>15</sup> sulfuric acid/water<sup>16</sup> and hydrochloric acid.<sup>1</sup> For this research, a procedure described in a patent was used to prepare the trichloride (**I**).<sup>17</sup> This method uses a mixture of sulfuric acid and glacial acetic acid and the product is allowed to precipitate from the reaction mixture (Eq 2.1). The crude product was pinkish-purple in color and obtained in greater than 97 % yield. Further purification could be obtained by recrystallizing from ethanol/water to give a 75 % yield. The trichloride (**I**) was used without further purification to prepare bisphenol C monomer (**II**). The trichloride (**I**) was recrystallized twice from an ethanol/water mixture to give transparent crystals before using it as a monomer. If compound **I** was exposed to air for a period of time the crystals would become light pink in color.



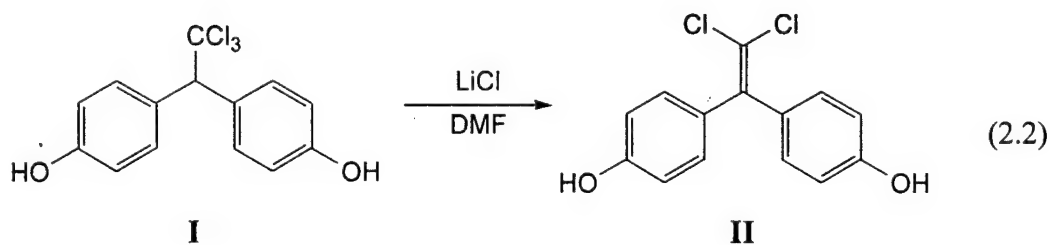


The trichloride has been successfully dehydrohalogenated by an number of methods including alcoholic KOH,<sup>18</sup> LiCl in dimethylformamide,<sup>2</sup> ammonia,<sup>19</sup> and methylamine.<sup>20</sup> While methanolic KOH has been the most widely used method for dehydrohalogenation, there are many by-products from the process, including 4,4'-dihydroxybenzil, bis(4-hydroxyphenyl)acetylene and 2,2-bis(4-hydroxyphenyl)-acetic acid and its methyl ester<sup>21</sup> (Figure 2.2). For this research, the trichloride was dehydro-



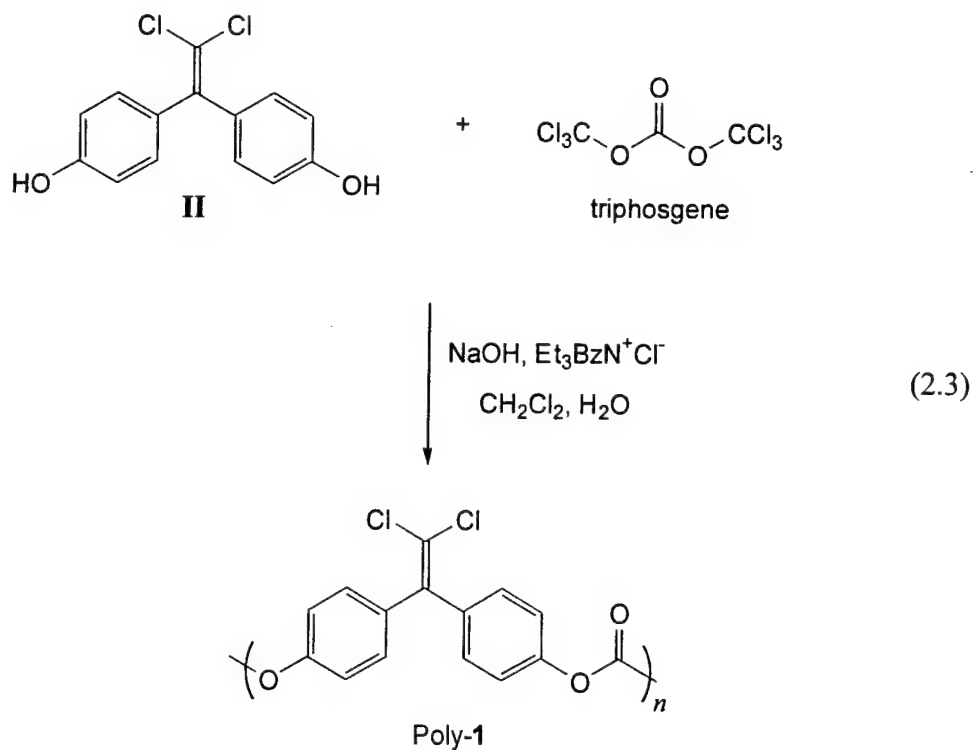
**Figure 2.2** Impurities identified from dehydrohalogenation of trichloride with alcoholic sodium hydroxide.<sup>21</sup>

halogenated by heating at reflux in dimethylformamide with lithium chloride as the catalyst (Eq 2.2). This method has been reported to give a much purer product.<sup>2</sup> The bisphenol C product was obtained as a fine crystalline solid in yields greater than 90 % after purification.



The first polycarbonate prepared from bisphenol C was reported in 1964 by a Polish research group.<sup>22</sup> Subsequent research was done by workers at General Electric on improving monomer and polymer synthesis in order to obtain polymers with good mechanical properties in addition to the flame-resistant properties.<sup>2,13,17,19</sup> Both groups used an interfacial polymerization technique with phosgene to prepare the polycarbonate from bisphenol C (II). We chose to use triphosgene as a phosgene substitute because the use of triphosgene is much more practical on a small laboratory scale (Eq. 2.3). Sun *et al.* has shown that high-molecular-weight polycarbonates can be obtained by both interfacial and solution polycondensation of bisphenols with triphosgene.<sup>23</sup> Triphosgene is hydrolytically unstable. Therefore, starting with a dry solvent is necessary in order to get reasonable molecular weights unless a large excess is used. The procedure used to make polycarbonate called for the addition of triphosgene in two steps. First, a stoichiometric amount of triphosgene was allowed to react with the bisphenolate anion for 15 minutes to form oligomers. A second addition of excess triphosgene was added to form high-molecular-weight polymer. This type of sequential addition is common when using monomers that are rapidly hydrolyzed by water.<sup>24</sup>

Polyarylates can be polymerized by a number of methods, including reaction of dicarboxylic acids with diphenol, dicarboxylic acids with diacetate of diphenol, ester of dicarboxylic acid with diphenol, and diacid chloride with diphenol.<sup>25,26</sup> From a commercial standpoint, polyarylates are generally prepared from the diacetate route because of cost, but this process requires high temperatures (200-350°C) and the removal of the acetic acid by-product can be difficult. Because of questions of the stability of



bisphenol C (**II**) at high temperatures, we choose to use an interfacial technique to prepare polyarylates (Eq. 2.4). The first polyarylates prepared from **II** were done so using a technique described in the patent literature.<sup>27</sup> For these first polymers (and copolymers with bisphenol A), the ratio of terephthaloyl and isophthaloyl groups was 3 to 1. For polyarylates prepared from bisphenol A with terephthaloyl and isophthaloyl groups, it has been found that the closer to equal amounts of both groups, the lower the crystallinity and the greater the solubility.<sup>28</sup> Later, to improve the solubility of the bisphenol C polyarylates, the ratio of terephthaloyl to isophthaloyl groups was changed to 1 to 1. While Brzozowski *et al.* described allowing the polymerizations to react for 3 hours,<sup>27</sup> most reports indicate that high-molecular-weight polymers can be obtained in



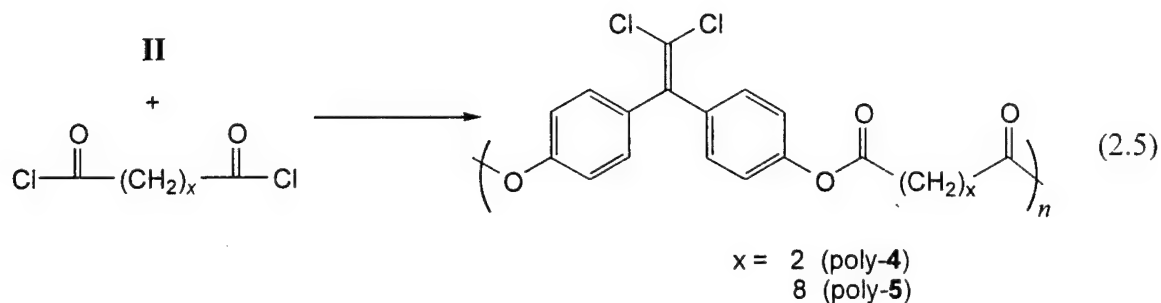
terephthaloyl to isophthaloyl groups and had gelled from the polymer reaction mixture. The bisphenol C polyarylate where the ratio of terephthaloyl to isophthaloyl groups is 1 to 1 was found to be much more soluble in chlorinated solvents, but there was still a small amount of gelled particles that would not dissolve.

Polyarylates prepared from bisphenol C and terephthaloyl chloride precipitated from the polymerization solution very rapidly (less than 2 minutes) as a fine white precipitate. These polymers exhibit a crystalline melting peak at 365 °C but no glass transition temperature.

Copolymers with varying ratios of bisphenol C to bisphenol A were prepared (Table 2.1). In all cases the amount of bisphenol C incorporated was that which was expected when measured using elemental analysis. Copolymers had better solubility than either of the homopolymers of either bisphenol C or bisphenol A. Aliphatic polyesters were also prepared from bisphenol C and succinyl and sebacoyl chlorides (Eq. 2.5). The aliphatic polyester from sebacoyl chloride was prepared in the same manner as the polyarylates, but the polymer was difficult to precipitate. The isolated product was sticky but dried into a clear solid. This initially amorphous polymer began to crystallize after

**Table 2.1** Copolyarylates prepared from bisphenol C and bisphenol A.

Sample	Ratio of BPC to BPA (mole fraction)	Amount of Chlorine (wt %)	Theoretical Amount of Chlorine (wt %)	Weight Percent of BPC Relative to BPA (wt %)
poly-14	100 / 0	16.73	17.30	100
poly-15	75 / 25	12.89	13.39	77
poly-16	50 / 50	8.97	9.23	53
poly-17	25 / 75	4.70	4.80	28
poly-18	0 / 100	0	0	0



standing at room temperature for several months. Succinyl chloride is much more moisture-sensitive than the sebacoyl chloride. The succinyl chloride was added in two stages. The polymer solution became discolored (brownish) during the course of the reaction, but once the polymer was precipitated and dried, it was only slightly tan.

Several other polyarylates and polyesters were also prepared as described above. The structure of each of the polymers is shown in Appendix A. The decomposition behavior and the combustion properties of the polymers will be discussed in Chapter 3.

## 2.3 Experimental Section

### 2.3.1 General Procedures and Characterizations

Infrared spectra were obtained using a Perkin-Elmer 1600 Series FTIR spectrometer. Polymer films were cast on NaCl disks and dried under vacuum. IR data are reported as absorbance in units of wavenumber ( $\text{cm}^{-1}$ ). The band strength is reported in parentheses with w = weak, m = medium and s = strong.

$^1\text{H}$  NMR and  $^{13}\text{C}\{^1\text{H}\}$  proton decoupled NMR spectra were obtained at 300 MHz and 75 MHz with a Bruker MSL-300 spectrometer. Chemical shifts for  $^1\text{H}$  NMR spectra

are reported in  $\delta$  (ppm), positive values indicating shifts downfield from tetramethylsilane (TMS). Chemical shifts are referenced to proton peaks of the solvent ( $\text{CD}_2\text{Cl}_2$ , 5.32, triplet;  $d_6$ -acetone, 2.05, quintet). Chemical shifts for  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra are reported in  $\delta$  (ppm), positive values indicating downfield shifts from TMS. Peaks were referenced to the solvent ( $\text{CDCl}_3$ , 77.23, triplet).

Elemental analyses were obtained on a Control Equipment Model 240XA elemental analyzer at the Microanalytical Laboratory Research Services, Graduate School, University of Massachusetts-Amherst.

Differential scanning calorimetry (DSC) thermograms were obtained with a TA Instruments DSC 2910. All measurements were made at a heating rate of  $10\text{ }^\circ\text{C}/\text{minute}$  under nitrogen atmosphere unless otherwise noted. The glass transition temperatures ( $T_g$ ) are taken from the second scans.

### 2.3.2 Reagents

Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. Isophthaloyl and terephthaloyl chlorides were recrystallized from hexane and stored under argon until use. Succinyl chloride was distilled under reduced pressure and stored under nitrogen. 4,4'-(Hexafluoroisopropylidene)diphenol (Bisphenol AF) was recrystallized from benzene and 4,4'-isopropylidenebis(2,6-dibromophenol) and 4,4'-isopropylidenebis(2,6-dichlorophenol) were recrystallized from toluene. 2,6-Dibromo-terephthaloyl chloride and 2,4-dibromo-isophthaloyl chloride were supplied by Dr. Jungsoo Kim of the University of

Massachusetts-Amherst. Naphthaloyl chloride was prepared according to a literature procedure.<sup>31</sup>

### 2.3.3 Monomer Synthesis

**1,1,1-Trichloroethylidene-2,2-bisphenol (I).** This bisphenol was synthesized using a procedure similar to described in the literature.<sup>17</sup> Chloral hydrate (104.2 g, 0.63 mol), phenol (131.2 g, 1.39 mol), and glacial acetic acid (120 mL) were added to a large reaction kettle that was equipped with an addition funnel, mechanical stirrer and a thermometer. The reaction kettle was cooled using an ice bath. A 1:1 mixture containing 60 mL of both glacial acetic acid and concentrated sulfuric acid was added dropwise over the period of 90 minutes, at a rate slow enough to insure the temperature of the reaction does not rise above 15 °C. Next, 150 mL of concentrated sulfuric acid was added dropwise over the period of about 90 minutes. After stirring for 2 hours, the mixture was allowed to come to room temperature. After stirring overnight, a pinkish-purple precipitate formed. Ice was added to the reaction mixture to dilute to twice the volume. Precipitate was filtered and then washed with large amounts of water until neutral. The product was then dried under vacuum at 60°C overnight. Yield: 194 g (97 %). <sup>1</sup>H NMR (*d*<sub>6</sub>-acetone): 8.42 (s, 2H), 7.54 (d, 4H), 6.82 (d, 4H), 5.10 (s, 1H). <sup>13</sup>C NMR (*d*<sub>6</sub>-acetone): 157.83, 132.16, 130.73, 115.78, 104.16, 70.22.

**1,1-Dichloroethylidene-2,2-bisphenol (II).** This bisphenol was prepared according a procedure described in the patent literature.<sup>2</sup> Trichloride, **I**, (105 g, 0.33 mol), lithium chloride (7.0 g, 0.17 mol) and dimethylformamide (800 mL) were added to a reaction flask that was equipped with a reflux condenser and mechanical



stirrer. The mixture was heated overnight at 140 °C. The reaction mixture was allowed to cool to 100 °C and then 2300 mL of water was added. This mixture was then allowed to cool slowly overnight to 35 °C while maintaining the stirring. Once the reaction mixture was at room temperature, the precipitate was filtered off, washed with water, and dried under vacuum at 60°C overnight. Ninety-two grams (99 %) of crude product was obtained. The product was recrystallized from DMF/ water (1:1.2) by slow cooling from 90°C. The crystals were filtered, washed with water and dried under vacuum at 70°C overnight to yield 88 g (95 %) of product. IR (neat): 3258 (br m), 3199 (br m), 1607 (m), 1600 (m), 1590 (m), 1506 (s), 1438 (m), 1361 (w), 1342 (w), 1249 (s), 1230 (s), 1210 (s), 1113 (w), 1100 (w), 1015 (w), 975 (m), 863 (m), 850 (w), 837 (m), 774 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $d_6$ -acetone): 8.56 (s, 2H), 7.13 (d, 4H), 6.83 (d, 4H).  $^{13}\text{C}$  NMR ( $d_6$ -acetone): 158.19, 141.98, 131.93, 131.64, 117.09, 115.91. Anal. Calcd for  $\text{C}_{14}\text{H}_{10}\text{O}_2\text{Cl}_2$ : C, 59.81; H, 3.59; Cl, 25.22. Found: C, 59.74; H, 3.55; Cl, 25.00.

**1-Chloroethylidene-2,2-bisphenol (III).** Compound **III** was prepared using a procedure similar to that described in the literature.<sup>32</sup> Phenol (12.37 g, 0.13 mol), chloroacetaldehyde diethyl acetal, (9.8 mL, 0.066 mol) and glacial acetic acid (24.6 mL) were added to a round bottom flask. The flask was cooled to below 5 °C using an ice bath. Sulfuric acid (4.4 mL) in glacial acetic acid (5.5 mL) was added dropwise over the period of 90 minutes and then the reaction mixture was stirred for 6 hours while maintaining the temperature below 5 °C. Next, the reaction mixture was poured into ice water and extracted with diethyl ether. The separated organic layer was washed twice with water and dried with magnesium sulfate. The ether was removed under reduced pressure and residual acetic acid and ethyl acetate were removed under high vacuum. The

product was recrystallized from benzene to yield 7.2 g (44 %).  $^1\text{H}$  NMR ( $d_6$ -acetone): 8.20 (br s, 2H), 7.15 (d, 4H), 6.78 (d, 4H), 4.16 (tr, 1H), 4.06 (d, 2H).

**4,4'-Dihydroxystilbene (IV)** 1-Chloroethylidene-2,2-bisphenol (**III**) (2.1 g, 0.0083 mol), dimethylformamide (19.1 mL) and lithium chloride (0.16 g, 0.0038 mol) were added to a reaction flask that was equipped with a reflux condenser and a mechanical stirrer. The reaction mixture was heated to 150 °C for 6 hours. This reaction mixture was allowed to cool to below 100 °C and then 27 mL of water was added. The reaction mixture was allowed to cool slowly overnight while maintaining the stirring. The resulting white precipitate was filtered and then dried under vacuum. The product was recrystallized from acetic acid to yield 0.73 g (42 %).  $^1\text{H}$  NMR ( $d_6$ -acetone):  $\delta$  8.39 (s, 2H), 7.40 (d, 4H), 6.92 (s, 2H), 6.83 (d, 4H).

**Ester from bisphenol C and benzoyl chloride (V).** Compound **II** (1.22 g, 0.0043 mol) and 20 mL of a 0.5 N NaOH solution were mixed in an Erlenmeyer flask. A solution of benzoyl chloride (1.21 g, 0.0086 mol) in 20 mL of  $\text{CH}_2\text{Cl}_2$  was added to the aqueous solution. The mixture was stirred for 30 minutes and then poured into hexane. The separated organic layer was washed with water (1 x 100 mL) and dried with  $\text{MgSO}_4$ . The solvents were removed using a rotary evaporator to yield a white solid. The product was recrystallized from a toluene/methanol mixture to yield large transparent crystals.  $^1\text{H}$  NMR ( $d_6$ -acetone): 8.19 (d, 4H), 7.74 (t, 2H), 7.60 (t, 4H), 7.51 (d, 4H), 7.38 (d, 4H). IR (neat): 3444 (w), 1735 (s), 1599 (m), 1584 (w), 1502 (m), 1451 (w), 1406 (w), 1263 (s), 1202 (s), 1165 (s), 1079 (m), 1060 (s), 1024 (m), 972 (w), 863 (m), 772 (w), 705 (m), 680 (w)  $\text{cm}^{-1}$ .

### 2.3.4 Polymer Synthesis

**Polycarbonate of bisphenol C (poly-1).** A procedure similar to that as described in the literature was used.<sup>23</sup> To an Erlenmeyer flask, 2.81 g (0.0100 mol) of 1,1-dichloroethylidene-2,2-bisphenol (**II**), 0.979g (0.0033 mol) of triphosgene, 0.020 g (0.0877 mmol) of benzyltriethylammonium chloride and 40 mL of dry CH<sub>2</sub>Cl<sub>2</sub> was added. The resulting dispersion was then added to a rapidly stirring solution of 1 N NaOH that was cooled with an ice bath. The mixture was stirred for 15 min, and then a solution of triphosgene (0.15 g, 0.005 mol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to the flask. After stirring the mixture for 45 min, dilute HCl was added dropwise until the mixture was acidic. The mixture was stirred for another 45 minutes, at which time the stirring was stopped and the ice bath removed. The aqueous and organic layers were separated, and the organic layer was washed with water several times until a neutral solution was obtained. The washings were done by rapidly stirring water with the polymer solution and then allowing the emulsion to stand until separated. To the resulting polymer solution, 100 mL of CH<sub>2</sub>Cl<sub>2</sub> was added, and this viscous polymer solution was poured into rapidly stirring methanol to precipitate the polymer. The resulting polymer was dried under vacuum at 60 °C overnight (yield = 2.35 g, 76 %).

DSC:  $T_g = 157^\circ\text{C}$ . IR (neat): 3482 (w), 3040 (w), 2962 (w), 1899 (w), 1774 (s), 1600 (m), 1504 (s), 1408 (m), 1223 (s), 1188 (s), 1160 (s), 1104 (m), 1017 (s), 974 (m), 888 (w), 861 (s), 802 (m), 768 (m), 710 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.37 (d), 7.28 (d). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 151.70, 150.63, 138.49, 137.32, 131.01, 121.01, 120.91.

Anal. Calcd for C<sub>15</sub>H<sub>8</sub>O<sub>3</sub>Cl<sub>2</sub>: C, 56.60; H, 2.61; Cl, 23.13. Found: C, 57.87; H, 2.39; Cl, 23.31.

### **Polyarylate from bisphenol C and terephthaloyl and isophthaloyl chlorides**

**(1:1) (poly-2).** In an Erlenmeyer flask, NaOH (1.0 g, 0.0025 mol) in 50 mL of water and bisphenol C (2.81 g, 0.001 mol) were mixed. Once the bisphenol C was dissolved, a solution of benzyltriethylammonium chloride (0.275 g, 1.2 mmol) of in 10 mL of water was added to the flask. One gram (0.005 mol) of both terephthaloyl and isophthaloyl chloride was dissolved in 25 mL of methylene chloride, and this was then added to the rapidly stirring bisphenolate solution. The mixture was stirred for 5 min, at which point, the organic phase was viscous but had not yet gelled. The mixture was poured into rapidly stirring acetone (300 mL) to precipitate the polymer. The isolated polymer was mixed well with 200 mL of water in a blender, filtered and dried overnight in a vacuum oven at 60 °C (yield = 3.74 g, 91 %). DSC:  $T_g = 216^\circ\text{C}$ . IR (neat): 3040 (w), 1899 (w), 1740 (s), 1600 (m), 1577 (m), 1504 (s), 1435 (w), 1408 (m), 1297 (s), 1260 (s), 1242 (s), 1199 (s), 1165 (s), 1077 (s), 1016 (s), 973 (m), 943 (w), 908 (m), 864 (s), 821 (m), 773 (m), 720 (s), 657 (w), 614 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 8.97 (s), 8.26 (d), 8.33 (s), 7.72 (t), 7.44 (d), 7.29 (d).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 164.14, 164.08, 150.51, 138.82, 137.16, 137.11, 135.27, 133.95, 131.00, 130.52, 130.29, 129.40, 121.70, 120.60. Anal. Calcd for  $\text{C}_{22}\text{H}_{12}\text{O}_4\text{Cl}_2$ : C, 64.23; H, 2.92; Cl, 17.27. Found: C, 64.01; H, 2.74; Cl, 17.18.

### **Polyarylate of bisphenol A and terephthaloyl and isophthaloyl chlorides (1:1)**

**(poly-3).** Poly-3 was prepared by a similar procedure to that described for poly-2. The amounts of reagents used were 0.5 g (0.0125 mol) of NaOH, 25 mL of water, 1.14 g (0.005 mol) of bisphenol A, 0.138 g (0.605 mmol) of benzyltriethylammonium chloride, 0.5 g (0.0025 mol) of terephthaloyl chloride, 0.5 g (0.0025 mol) of isophthaloyl chloride and 17 mL of methylene chloride. The polymerization mixture was stirred for 10 min

before precipitating the polymer by pouring the mixture into acetone (200 mL) in a blender. The polymer was isolated and then mixed well in a blender with water (200 mL), filtered and dried (yield = 1.56 g, 87 %). DSC:  $T_g = 209\text{ }^{\circ}\text{C}$ . IR (neat): 3038 (w), 2967 (m), 2872 (w), 1898 (w), 1739 (s), 1603 (m), 1591 (w), 1577 (w), 1504 (s), 1464 (w), 1435 (w), 1407 (m), 1386 (w), 1363 (m), 1298 (s), 1262 (s), 1244 (s), 1202 (s), 1170 (s), 1071 (s), 1015 (s), 954 (m), 905 (w), 872 (m), 811 (m), 786 (w), 770 (w), 721 (s), 676 (w), 645 (w), 631 (w), 551 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 8.96 (d), 8.44 (d), 8.32 (s), 7.70 (t), 7.36 (d), 7.18 (d), 1.76 (s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 164.55, 164.50, 148.83, 148.44, 148.37, 135.10, 134.11, 131.94, 130.51, 130.45, 129.25, 128.20, 121.18, 42.81, 31.19.

**Polyester from bisphenol C and succinyl chloride (poly-4).** In an Erlenmeyer flask, NaOH (0.45 g, 0.011 mol) in 23 mL of water and bisphenol C (**II**) (1.27 g, 0.0045 mol) were mixed. Once the bisphenol C was dissolved, benzyltriethylammonium chloride (0.125 g, 0.0005 mol) was added to the flask. Using air-free techniques, a solution of succinyl chloride (0.5 mL, 0.0045 mol) in anhydrous methylene chloride (15 mL) was prepared in a dry flask. The acid chloride solution was added to the rapidly stirring bisphenolate solution. After stirring for 15 min, a solution of succinyl chloride (0.25 mL, 0.0022 mol) in methylene chloride (5 mL) was added dropwise to the flask. Dilute  $\text{NaOH}_{\text{aq}}$  was added to polymer reaction to keep solution basic. The mixture was stirred for 10 minutes and then precipitated into acetone. The polymer gelled in acetone, but upon mixing well in a blender, it was possible to precipitate the polymer. The polymer was filtered, blended with water and dried under vacuum at  $60\text{ }^{\circ}\text{C}$  for several days. The final product was tan when still wet, but after drying it was an off-

white solid (yield = 1.6 g, 95 %). DSC:  $T_g = 117\text{ }^\circ\text{C}$ . IR (neat): 3039 (w), 1757 (s), 1600 (w), 1576 (w), 1505 (m), 1407 (m), 1358 (m), 1309 (w), 1201 (s), 1166 (s), 1128 (s), 1018 (m), 974 (m), 946 (w), 917 (w), 888 (w), 864 (m), 840 (w), 774 (w), 734 (w).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 7.31 (d, 4H), 7.10 (d, 4H), 2.97 (s, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 171.16, 150.87, 139.42, 137.34, 131.04, 122.09, 120.68, 29.75.

**Polyester from bisphenol C and sebacoyl chloride (poly-5).** In an Erlenmeyer flask, NaOH (0.5 g, 0.0125 mol) in 25 mL of water and bisphenol C (**II**) (1.41 g, 0.005 mole) were mixed. Once the bisphenol C was dissolved, a solution of benzyltriethylammonium chloride (0.1375 g, 0.0006 mol) in 17.5 mL of water was added to the flask. A solution of sebacoyl chloride (1.06 mL, 0.005 mol) in methylene chloride (50 mL) was prepared and this solution was added to the rapidly stirring bisphenolate solution. After stirring the mixture for 3 hours, methylene chloride (100 mL) was added to the flask and stirring was continued for another 30 min. The mixture was then acidified to pH = 1 using dilute  $\text{HCl}_{\text{aq}}$  and stirred for an additional 30 min. The aqueous and organic layers were separated and the organic layer was washed with water several times until a neutral solution was obtained. The washings were done by rapidly stirring water with the polymer solution and then allowing the emulsion to stand until separated. The resulting polymer solution was poured into rapidly stirring cold methanol ( $-60\text{ }^\circ\text{C}$ ) to precipitate the polymer. The resulting solid was tacky. The polymer was dried under vacuum for several days and then under high vacuum at room temperature. DSC (1<sup>st</sup> scan) m.p.  $49\text{ }^\circ\text{C}$ ; (2<sup>nd</sup> scan)  $T_g = 46\text{ }^\circ\text{C}$ . IR (neat): 3038 (w), 2929 (m), 2854 (m), 1900 (w), 1758 (s), 1648 (w), 1601 (m), 1577 (w), 1505 (s), 1465 (w), 1408 (w), 1362 (w), 1296 (w), 1260 (m), 1203 (s), 1165 (s), 1119 (s), 1018 (s), 974 (m), 946 (w),

919 (w), 864 (m), 800 (m), 710 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 7.31 (d, 4H), 7.07 (d, 4H), 2.54 (t, 4H), 1.74 (m, 4H), 1.38 (br, 8H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 172.17, 150.53, 139.01, 136.70, 130.78, 121.62, 120.17, 34.53, 29.24, 29.18, 25.02. Anal. Cal'd.:  $\text{C}_{24}\text{H}_{24}\text{O}_4\text{Cl}_2$ : C, 64.43; H, 5.37; Cl, 15.88. Found: C, 64.38; H, 5.46; Cl, 15.71.

**Polyester from bisphenol A and sebacoyl chloride (poly-6).** Poly-6 was prepared using the same procedure as described poly-5. The amounts of reagents used were 0.5 g (0.0125 mol) of sodium hydroxide, 25 + 17.5 mL of water, 1.41 g (0.005 mol) of bisphenol A, 0.1375 g (0.0006 mol) of benzyltriethylammonium chloride, 1.06 mL (0.005 mol) of sebacoyl chloride, 50 + 200 mL of methylene chloride. The resulting tacky polymer was dried for several days under vacuum. DSC:  $T_g = 28\text{ }^\circ\text{C}$ . IR (neat): 3037 (w), 2930 (s), 2855 (m), 1756 (s), 1602 (w), 1590 (w), 1505 (s), 1464 (w), 1410 (w), 1363 (m), 1289 (w), 1206 (s), 1170 (s), 1140 (s), 1080 (s), 1016 (m), 920 (m), 845 (m), 730 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 7.24 (d, 4H), 6.97 (d, 4H), 2.53 (t, 4H), 1.68 (m, 4H), 1.38 (m, 8H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 172.57, 148.80, 147.96, 127.99, 121.11, 42.65, 34.56, 31.15, 29.27, 29.21, 26.09.

**Polyarylate from tetrabromobisphenol A and terephthaloyl and isophthaloyl chlorides (1:1) (poly-7).** Poly-7 was prepared by a similar procedure to that described for poly-2. The amounts of reagents used were 0.5 g (0.0125 mol) of sodium hydroxide, 25 mL of water, 2.7 g (0.0045 mol) of bisphenol AF, 0.1375 g (0.0006 mol) of benzyltriethylammonium chloride, 0.50 g (0.0025 mol) of terephthaloyl chloride, 0.50 g (0.0025 mol) of isophthaloyl chloride and 17 mL of methylene chloride. The polymerization mixture was stirred for 5 min before precipitating the polymer by pouring the mixture into acetone (200 mL) in a blender. The polymer was isolated and then

mixed well in a blender with water (200 mL), filtered and dried (yield = 3.0, 90 %).

DSC:  $T_g = 277\text{ }^{\circ}\text{C}$ . IR (neat): 2970 (m), 1757 (s), 1608 (w), 1584 (w), 1550 (m), 1456 (m), 1408 (w), 1390 (m), 1289 (w), 1232 (s), 1171 (m), 1108 (w), 1065 (s), 1049 (s), 1013 (s), 953 (w), 871 (m), 808 (w), 744 (m), 714 (m), 686 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 9.06 (s), 8.57 (d), 8.41 (s), 7.78 (t), 7.53 (s), 1.72 (s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 162.36, 162.26, 149.99, 144.72, 135.88, 133.27, 132.74, 131.04, 129.63, 129.46, 117.92, 117.86, 43.02, 30.77.

**Polyarylate from tetrachlorobisphenol A and terephthaloyl and isophthaloyl chlorides (1:1) (poly-8).** Poly-8 was prepared by a similar procedure to that described for poly-2. The amounts of reagents used were 0.5 g (0.0125 mol) of sodium hydroxide, 25 mL of water, 1.8 g (0.005 mol) of tetrabromobisphenol A, 0.1375 g (0.0006 mol) of benzyltriethylammonium chloride, 0.5 g (0.0025 mol) of terephthaloyl chloride, 0.5 g (0.0025 mol) of isophthaloyl chloride and 17 mL of methylene chloride. The polymerization mixture was stirred for 8 min before precipitating the polymer by pouring the mixture into acetone (200 mL) in a blender. The polymer was then isolated and then mixed well in a blender with water (200 mL), filtered and dried (yield = 2.0, 83 %).

DSC:  $T_g = 261\text{ }^{\circ}\text{C}$ . IR (neat): 2971 (m), 2876 (w), 1757 (s), 1608 (w), 1588 (w), 1563 (m), 1470 (s), 1408 (w), 1396 (m), 1280 (m), 1250 (s), 1237 (s), 1199 (s), 1172 (w), 1137 (w), 1117 (w), 1081 (s), 1050 (s), 1014 (s), 953 (w), 889 (w), 870 (m), 809 (m), 715 (m), 688 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) 9.05 (s), 8.56 (d), 8.41 (s), 7.78 (t), 7.35 (s), 1.7 (s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 162.45, 162.35, 149.20, 149.14, 142.45, 135.91, 133.11, 132.70, 130.96, 129.63, 129.29, 129.00, 127.35, 43.24, 30.63.



### **Polyarylate of bisphenol AF and terephthaloyl and isophthaloyl chlorides**

**(1:1) (poly-9).** Poly-9 was prepared by a similar procedure to that described for the poly-2. The amounts of reagents used were 0.43 g (0.0125 mol) of sodium hydroxide, 25 mL of water, 1.5 g (0.0045 mol) of bisphenol AF, 0.122 g (0.0005 mol) of benzyltriethylammonium chloride, 0.45 g (0.0022 mol) of terephthaloyl chloride, 0.45 g (0.0022 mol) of isophthaloyl chloride and 13 mL of methylene chloride. The polymerization mixture was stirred for 20 min before precipitating the polymer by pouring the mixture into acetone (200 mL) in a blender. The polymer was isolated and then mixed well in a blender with water (200 mL) and filtered. Some of the resulting tacky polymer stuck to the filter paper. The polymer that was isolated was dried overnight under vacuum at 60 °C (yield = 1.7 g, 83 %). The resulting polymer was not tacky. DSC:  $T_g = 229^\circ\text{C}$ . IR (neat): 3081 (w), 2923 (w), 1744 (s), 1606 (w), 1511 (m), 1408 (w), 1296 (w), 1259 (s), 1241 (s), 1207 (s), 1175 (s), 1066 (m), 1016 (m), 969 (w), 955 (w), 938 (w), 872 (w), 808 (w), 720 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 8.99 (s), 8.48 (d), 8.35 (s), 7.74 (t), 7.54 (d), 7.35 (d).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 164.00, 163.94, 151.36, 135.44, 133.93, 132.09, 131.85, 131.24, 131.19, 130.64, 130.21, 129.52, 121.74.

**Polyarylate from 4,4'-dihydroxystilbene and terephthaloyl and isophthaloyl chloride (1:1) (poly-10).** Poly-10 was prepared by a similar procedure to that described for the poly-2. The amounts of reagents used were 0.24 g (0.006 mol) of sodium hydroxide, 11 mL of water, 0.5 g (0.0024 mol) of 4,4'-dihydroxystilbene (**IV**), 0.065 g (0.0003 mol) of benzyltriethylammonium chloride, 0.24 g (0.0012 mol) of terephthaloyl chloride, 0.24 g (0.0012 mol) of isophthaloyl chloride and 10 mL of methylene chloride. The product precipitated from the mixture in less than one minute as hard solid chunks.

The reaction mixture was mixed with acetone (100 mL) in a blender. The polymer was isolated and then mixed well in a blender with water (100 mL), filtered and dried to give a yellow solid (yield = 0.66 g, 83 %).

**Polyarylate from trichloride and terephthaloyl and isophthaloyl chlorides**

**(1:1) (poly-11).** Poly-11 was prepared by a similar procedure to that described for poly-2.

The amounts of reagents used were 0.5 g (0.0125 mol) of NaOH, 25 mL of water, 1.6 g (0.005 mol) of trichloride, 0.1375 g (0.0006 mol) of benzyltriethyl-ammonium chloride, 0.5 g (0.0025 mole) of terephthaloyl chloride, 0.5 g (0.0025 mole) of isophthaloyl chloride and 17 mL of methylene chloride. The polymerization mixture was stirred for 10 min before precipitating the polymer by pouring the mixture into acetone (200 mL) in a blender. The polymer was isolated and then mixed well with water (200 mL), filtered and dried (yield=1.98 g, 88 %). DSC:  $T_g = 252\text{ }^{\circ}\text{C}$ . IR (neat): 3467 (w), 3074 (w), 3041 (w), 1898 (w), 1740 (s), 1604 (m), 1577 (w), 1506 (s), 1435 (w), 1408 (m), 1296 (s), 1261 (s), 1242 (s), 1204 (s), 1168 (s), 1112 (m), 1077 (s), 1016 (s), 954 (w), 896 (w), 871 (m), 818 (m), 753 (m), 720 (s), 666 (w), 618 (m), 597 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 8.96 (s), 8.45 (d), 8.32 (s), 7.75 (d), 7.29 (d), 5.23 (s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 164.13, 164.08, 150.55, 135.90, 135.84, 135.25, 133.97, 131.98, 131.51, 130.52, 129.38, 121.65, 101.37, 69.93. Anal. Cal'd for  $\text{C}_{22}\text{H}_{13}\text{O}_4\text{Cl}_3$ : C, 58.99; H, 2.91; Cl, 23.90. Found: C, 58.76; H, 2.76; Cl, 23.58.

**Polyarylate from bisphenol C and naphthaloyl chloride (poly-12).** Poly-12

was prepared by a similar procedure to that described for poly-2. The amounts of reagents used were 0.2 g (0.0125 mol) of NaOH, 15 mL of water, 0.5 g (0.0018 mol) of bisphenol C (**II**), 0.055 g (0.0002 mol) of benzyltriethylammonium chloride, 0.45 g

(0.0018 mol) of naphthaloyl chloride and 30 mL of methylene chloride. The polymer precipitated from the mixture within 4 minutes as a fine precipitate. The reaction mixture was mixed with acetone (100 mL) in a blender. The polymer was isolated and then mixed well in a blender with water (100 mL), filtered and dried (yield=0.73 g, 89 %).

**Polyarylate from bisphenol C and 2,5-dibromo-terephthaloyl and 2,4-dibromo-isophthaloyl chlorides (1:1) (poly-13).** Poly-13 was prepared by a similar procedure to that described for poly-2. The amounts of reagents used were 0.28 g (0.0069 mol) of NaOH, 25 mL of water, 0.77 g (0.0027 mol) of bisphenol C, 0.076 g (0.0003 mol) of benzyltriethylammonium chloride, 0.50 g (0.0014 mol) of 2,5-dibromo-terephthaloyl chloride, 0.50 g (0.0014 mol) of 2,3-dibromo-isophthaloyl chloride and 12 mL of methylene chloride. The polymerization mixture was stirred for 20 min before precipitating the polymer by pouring the mixture into acetone (200 mL) in a blender. The polymer was isolated and then mixed well with water (200 mL), filtered and dried (yield = 1.4 g, 90 %). DSC:  $T_g = 207\text{ }^{\circ}\text{C}$ . IR (neat): 3092 (w), 3038 (w), 1901 (w), 1753 (s), 1599 (m), 1580 (m), 1538 (w), 1503 (s), 1464 (m), 1407 (m), 1340 (m), 1277 (m), 1261 (s), 1220 (s), 1196 (s), 1164 (s), 1098(m), 1042 (s), 974 (m), 953 (w), 912 (w), 864 (m), 819 (w), 772 (m), 759 (m), 712 (w), 670 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 8.67 (s), 8.33 (s), 8.20 (s), 7.42 (br d), 7.30 (br d).

**Polyarylate from Bisphenol C and terephthaloyl and isophthaloyl chlorides (3:1) (poly-14).** Poly-14 was made using a procedure described in the patent literature.<sup>27</sup> To an Erlenmeyer flask containing a magnetic stir bar, NaOH (0.5 g, 0.0025 mol) in 25 mL of water and bisphenol C (**II**) (1.4 g, 0.005 mols) were mixed. Once the

bisphenol C was dissolved, a solution of benzyltriethylammonium chloride (0.1375 g, 0.0006 mol) in 12.5 mL of water was added to the flask. Terephthaloyl chloride (0.75 g, 0.0037 mol) and isophthaloyl chloride (0.25 g, 0.0012 mol) were dissolved in 12.5 mL of methylene chloride, and this solution was added to the rapidly stirring bisphenolate solution. The polymerization mixture was stirred for 3 hours, at which time the polymer had precipitated from solution. Methylene chloride (50 mL) was added to the flask and stirring was continued for an additional 30 minutes. Dilute  $\text{HCl}_{\text{aq}}$  was then added dropwise until the mixture was acidic. The mixture was stirred for another 30 minutes, at which time the stirring was stopped and the organic and aqueous layers were separated. The organic layer was washed with water several times until a neutral solution was obtained. The washings were done by rapidly stirring water with the polymer solution and then allowing the emulsion to stand until separated. The polymer solution was poured into rapidly stirring cold methanol ( $-50\text{ }^{\circ}\text{C}$ ), filtered cold, and dried (yield = 1.9 g, 91 %). Anal. Calcd for  $\text{C}_{22}\text{H}_{12}\text{O}_4\text{Cl}_2$ : C, 64.26; H, 2.94; Cl, 17.24. Found: C, 64.09; H, 2.91; Cl, 16.73.

#### **Copolymers of bisphenol C and bisphenol A polyarylates.**

**C/A = 75/25 (mole %) (poly-15).** Poly-15 was prepared by the same procedure as described for poly-14. The quantities of reagents used were 0.5 g (0.013 mol) of sodium hydroxide, 25 + 17.5 mL of water, 1.1 g (0.0038 mol) of bisphenol C (**II**), 0.29 g (0.0013 mol) of bisphenol A, 0.14 g (0.0006 mol) of benzyltriethylammonium chloride, 0.75 g (0.0037 mol) of terephthaloyl chloride, 0.25 g (0.0012 mol) of isophthaloyl chloride and 12.5 + 50 mL of methylene chloride. Yield = 1.8 g (89 %). Anal. Calcd for  $\text{C}_{89}\text{H}_{54}\text{O}_{16}\text{Cl}_6$ : C, 67.14; H, 3.42; Cl, 13.68. Found: C, 67.08; H, 3.36; Cl, 12.89.

**C/A = 50/50 (mole %) (poly-16)** Poly-16 was prepared by the same procedure as described for poly-14. The quantities of reagents used were 0.5 g (0.013 mol) of NaOH, 25 + 17.5 mL of water, 0.70 g (0.0025 mol) of bisphenol C, 0.57 g (0.0025 mol) of bisphenol A, 0.14 g (0.0006 mol) of benzyltriethylammonium chloride, 0.75 g (0.0037 mol) of terephthaloyl chloride, 0.25 g (0.0012 mol) of isophthaloyl chloride and 12.5 + 50 mL of methylene chloride. Yield = 1.7 g (88 %). Anal. Calcd for  $C_{45}H_{30}O_8Cl_2$ : C, 70.23; H, 3.93; Cl, 9.21. Found: C, 70.00; H, 3.91; Cl, 8.97.

**C/A = 25/75 (mole %) (poly-17)** Poly-17 was prepared by the same procedure as described for poly-14. The quantities of reagents used were 0.5 g (0.013 mol) of sodium hydroxide, 25 + 17.5 mL of water, 0.35 g (0.0013 mol) of bisphenol C (II), 0.86 g (0.0038 mol) of bisphenol A, 0.14 g (0.0006 mol) of benzyltriethylammonium chloride, 0.75 g (0.0037 mol) of terephthaloyl chloride, 0.25 g (0.0012 mol) of isophthaloyl chloride and 12.5 + 50 mL of methylene chloride. Yield = 1.7 g (91 %). Anal. Calcd for  $C_{91}H_{66}O_{16}Cl_2$ : C, 73.53; H, 4.48; Cl, 4.77. Found: C, 73.30; H, 4.64; Cl, 4.70.

**Polyarylate from Bisphenol A and terephthaloyl and isophthaloyl chlorides (3:1) (poly-18).** Poly-18 was prepared by the same procedure as described for poly-14. The quantities of reagents used were 1.0 g (0.025 mol) of sodium hydroxide, 50 + 35 mL of water, 2.28 g (0.010 mol) of bisphenol A, 0.14 g (0.0006 mol) of benzyltriethylammonium chloride, 1.5 g (0.0074 mol) of terephthaloyl chloride, 0.50 g (0.0025 mol) of isophthaloyl chloride and 25 + 100 mL of methylene chloride. Yield = 3.4 g (94 %). Anal. Calcd for  $C_{23}H_{18}O_4$ : C, 77.08; H, 5.06. Found: C, 76.84; H, 4.99.

**Polyarylate from Bisphenol C and terephthaloyl chloride.** This polymer was prepared by the same procedure as described for poly-14. The quantities of reagents used

were 0.5 g (0.013 mol) of NaOH, 25 + 17.5 mL of water, 1.4 g (0.0050 mol) of bisphenol C (**II**), 0.14 g (0.0006 mol) of benzyltriethylammonium chloride, 1.0 g (0.0049 mol) of terephthaloyl chloride and 12.5 + 50 mL of methylene chloride.

**Polyarylate from Bisphenol A and terephthaloyl chloride.** This polymer was prepared by the same procedure as described for poly-**14**. The quantities of reagents used were 0.5 g (0.013 mol) of NaOH, 25 + 17.5 mL of water, 1.1 g (0.0050 mol) of bisphenol C, 0.14 g (0.0006 mol) of benzyltriethylammonium chloride, 1.0 g (0.0049 mol) of terephthaloyl chloride and 12.5 + 50 mL of methylene chloride.

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## **CHAPTER 3**

# **DECOMPOSITION AND COMBUSTION BEHAVIOR OF BISPHENOL-C-BASED POLYMERS**

### **3.1 Introduction**

The degradation of polymers plays a significant role in the combustion process. The rate of degradation, the amount of degradation and the nature of the degradation products are all important parameters contributing to further burning. In this chapter, the results on the degradation of bisphenol C materials studied by a variety of techniques is presented. Also, the combustion properties of these polymers measured using microcalorimetry are reported.

### **3.2 Degradation Behavior of Polymers**

#### **3.2.1 Homopolymers**

While many bisphenol-C-based polymers have been synthesized, little research has been done on studying their thermal and decomposition behavior. Factor has reported on the presence of an exothermic decomposition reaction and high char yields from bisphenol C polymers.<sup>1</sup> Other researchers have reported a possible crosslinking reaction occurring at 150-200 °C that renders the polymers insoluble.<sup>2-4</sup> Polyurethane and polyurea resins containing dichloroethylidene functionality have been reported to show a distinct exotherm in the DSC trace followed by an endothermic decomposition reaction.<sup>5,6</sup> Whether this exotherm is from further curing of the resins or from a reaction

including the dichloroethylidene moiety was not addressed. In the following sections, results are described from the decomposition behavior of bisphenol C materials as studied using thermal analysis, spectroscopy and pyrolysis-GC/MS.

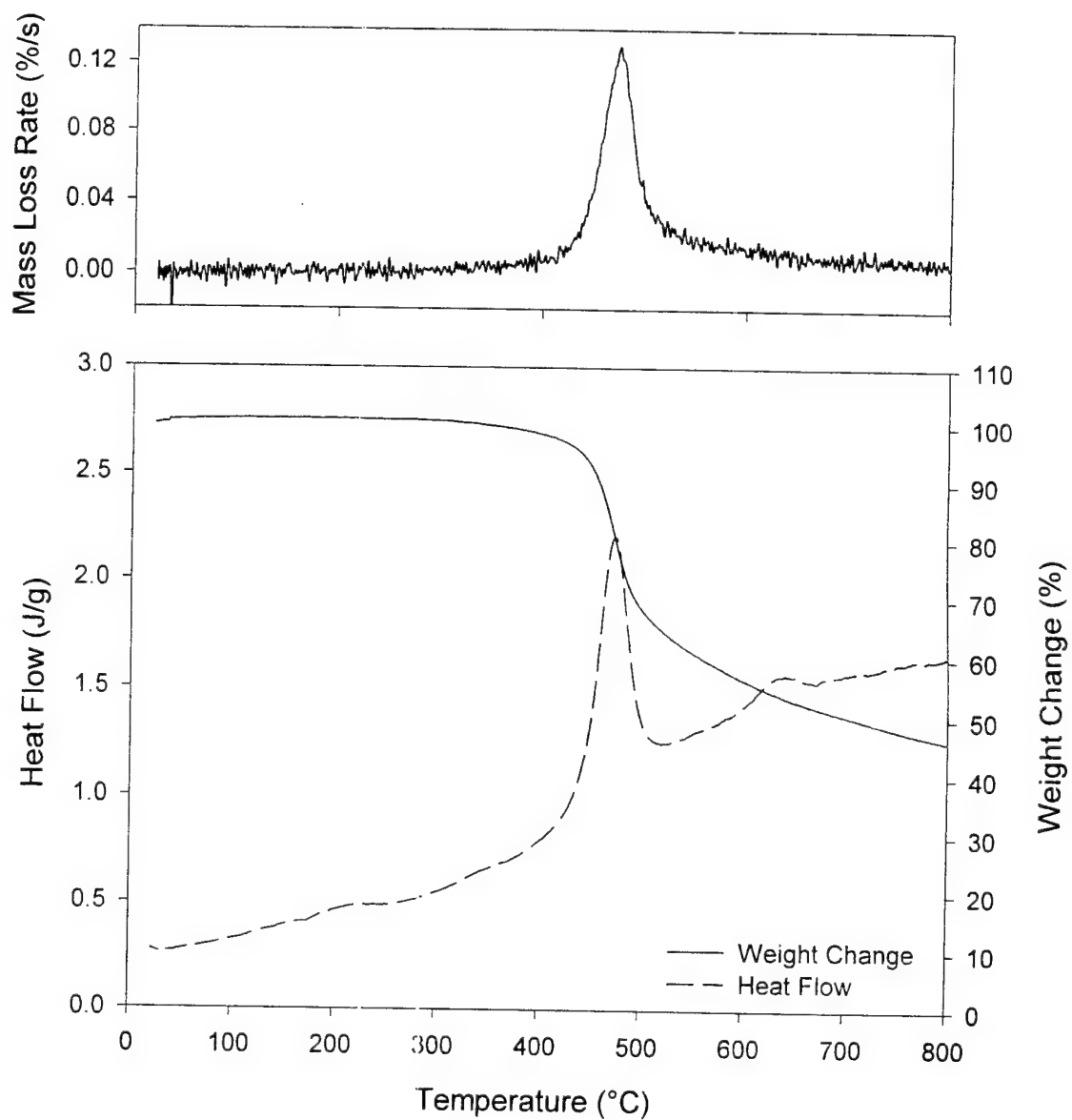
#### 3.2.1.1 Thermal Analysis

The degradation behavior of bisphenol C polymers was investigated using simultaneous thermogravimetry-differential scanning calorimetry (TGA-DSC), which will be referred to as STA. This technique allows for the measurement of the heat flow associated with decomposition reactions while monitoring the corresponding weight change. The decomposition behavior of polymers during flaming combustion is thought to be anaerobic with all of the atmospheric oxygen being consumed before reaching the decomposing polymer surface.<sup>7</sup> Therefore, the study of the decomposition behavior of polymers under inert atmosphere is relevant.

There is little data from STA experiments on polymers in the literature. Some of difficulty in obtaining reliable and reproducible DSC data from STA experiments comes from two sources. The first is the inherent problem of defining a baseline. Usually a baseline for a DSC trace is determined using two empty pans and the difference in heat flow between the two pans is used to calibrate the instrument, for differences between sample and reference locations. Once a sample is placed in the pan, the difference in baseline from that of the empty pans gives some measure of the heat capacity of the sample. Typically the use of DSC for polymers has been to investigate phase transitions or reactions that occur without weight change. For the study of the decomposition of polymers, the weight is changing and therefore the baseline is changing. For materials

that have well-defined weight change reactions or large heat flow reactions, it can be easier to determine a sample baseline. Many polymers have complex decomposition behavior with a series of exothermic and endothermic reactions occurring simultaneously. The second difficulty with the DSC data from the STA experiments is more of an equipment issue. The DSC cell in the Rheometrics STA 1500, which was used for this research, is suspended in the furnace from a balance. The fact that the DSC can swing freely affects the placement of the cell, which in turn can change the location of the reference and sample pan within the furnace. This free movement of the cell can cause considerable change in the baseline, requiring frequent and careful calibration.

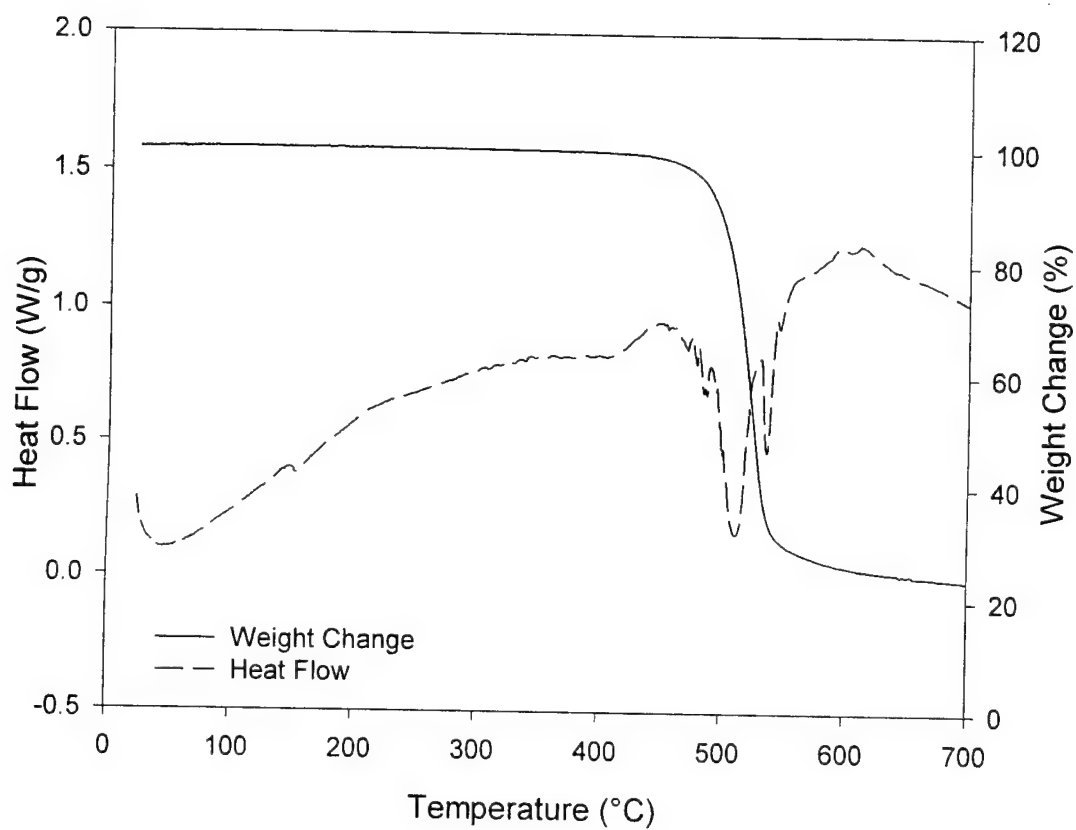
From the DSC curve of an STA experiment, it is possible to determine the heat of decomposition. Contributions to the heat of decomposition include the energy to break bonds, form new bonds and vaporize the decomposition products. Polymers typically decompose endothermically in the absence of oxygen.<sup>7</sup> This is probably due to the endothermic bond breaking and vaporization processes dominating the decomposition process. Normalization with respect to the initial mass is the typical way to report heat flow data from DSC. The measurement of heat flow during a weight loss can be normalized with respect to the initial mass or to the instantaneous mass. Unless otherwise stated, the DSC data from STA experiments is normalized to the initial mass. Figure 3.1 shows a STA thermogram for the decomposition of bisphenol C polycarbonate, poly-1. (A peak in the positive direction indicates an exothermic process). An exothermic reaction takes place in the region of 390-670 °C. The heat associated with the decomposition of poly-1 is  $+350 \pm 26$  J/g or 107 kJ/mol of repeat unit. For comparison, the decomposition behavior for bisphenol A polycarbonate (BPA-PC) is



**Figure 3.1** Simultaneous-TGA/DSC results for bisphenol C polycarbonate (poly-1).

shown in Figure 3.2. BPA-PC has an endothermic decomposition with a heat of around - 200 J/g. The decomposition of BPA-PC has several peaks in the DSC curve while the weight loss curve does not show corresponding changes in weight loss. For poly-1, there is one large exothermic peak. The temperature at the maximum in the exothermic peak corresponds to the temperature in the maximum in the rate of mass loss. The fact the maximum in the heat flow occurs at the same temperature as the maximum in the rate of weight loss indicates that either the same process is responsible for both observations or that one process causes the other to occur. For example, bond breaking leads to weight loss but the remaining polymer could contain reactive groups that might undergo an exothermic reaction.

All of the bisphenol C materials show exothermic decomposition behavior occurring with simultaneous weight loss. STA thermograms for the other bisphenol C materials examined are shown in Appendix C. Important data from the DSC and corresponding TGA traces is shown in Table 3.1 and Table 3.2, respectively. The heats of decomposition for the bisphenol C polymers range from 208 to 350 J/g based on the initial weight. If the heat of decomposition is figured per mole of repeat unit, the results range from 107 to 118 kJ/mole. When comparing bisphenol C polymers with bisphenol A analogs a few trends can be identified. Bisphenol C polymers decompose at lower temperatures, have higher char yields and lower peak mass loss rates (compare poly-1 with BPA-PC, poly-2 with poly-3, and poly-5 with poly-6). Also, all of the bisphenol C polymers decomposed in an exothermic manner, while the bisphenol A polymers decomposed in an endothermic fashion.



**Figure 3.2** Simultaneous-TGA/DSC results for bisphenol A polycarbonate.

**Table 3.1** Summary of DSC results from simultaneous-TGA/DSC experiments for bisphenol-C-based materials.

Sample	Temperature of Peak in Exotherm (°C)	Heat of Decomposition <sup>a</sup> (J/g)	Heat of Decomposition (kJ/mol)	Temperature Range <sup>b</sup> (°C)
poly-1	472 ± 2	350 ± 24	107	391-670
poly-2	472 ± 2	263 ± 33	108	415-605
poly-13	459 ± 3	208	118	395-785
poly-4	410 ± 4	330 ± 7	119	360-670
bisphenol C (II)	267 ± 2	152 ± 9	42.7	240-285

<sup>a</sup> Area under exothermic peak normalized with respect to the initial mass. <sup>b</sup> Temperature range over which exothermic transition occurs.

**Table 3.2** Summary of TGA results for bisphenol-C-containing materials and related polymers.

Sample	Onset of Decomposition <sup>a</sup> (°C)	Maximum Rate of Mass Loss (%/s)	Char Yield at 700 °C (%)	Temperature at Maximum Rate of Mass Loss (°C)
poly-1	439 ± 3	0.13	51 ± 0	472 ± 2
poly-2	455 ± 7	0.076	53 ± 1	476 ± 2
poly-5	360	0.13	34	383
poly-13	428 ± 6	0.099	39 ± 0	460 ± 1
poly-4	352 ± 9	0.16	41 ± 0	409 ± 4
II	246 ± 1	0.37	47 ± 1	262 ± 1
V	335	0.22	13	421
BPA-PC	454	0.25	19	485
poly-3	469	0.31	26	497
poly-6	403	0.34	3.5	445
poly-7	431	0.20	31	449
poly-8	461	0.19	40	479
poly-9	445	0.11	39	504

<sup>a</sup> Reported at a mass change of 5 wt%.

For poly-1, the initial mass loss is equal to 45 wt%. This loss is approximately equal to the weight percent of HCl and carbon dioxide that could be generated from the polymer. For poly-2 it is difficult to determine a defined weight loss step but it appears

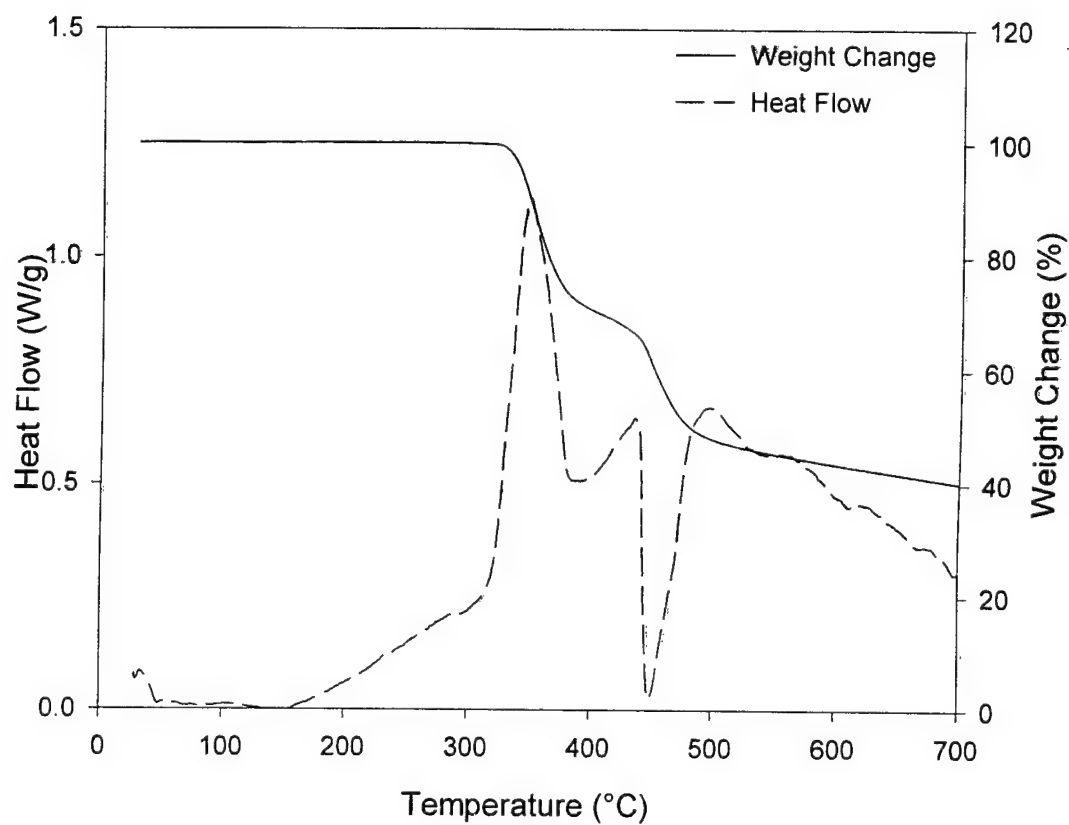
that the weight loss is greater than that of just the generation of HCl and carbon dioxide but not great enough to include the weight loss of all of the tere/isophthaloyl groups.

For poly-5, the polyester from sebacoyl chloride and bisphenol C, STA results of a freshly prepared polymer showed a distinct two-stage decomposition process (Figure 3.3). In the first stage, a large exothermic peak was observed, followed by an endothermic peak at which two different weight-loss steps take place. The temperature of the maximum in the DSC peaks corresponds the temperature of the maximum weight-loss rate.

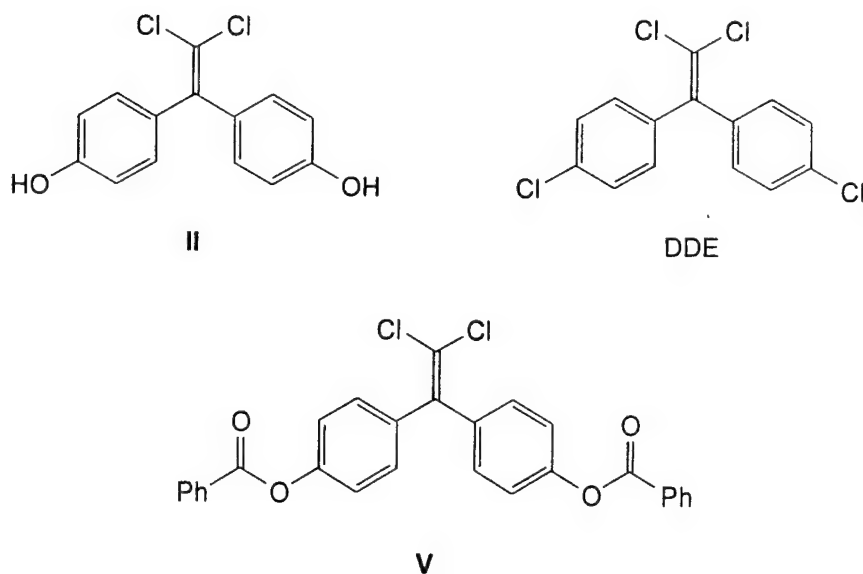
The STA results differed when poly-5 was tested after storing at room temperature for several months. The aged sample still had two decomposition steps, but the transitions were not nearly as distinct and the onset of decomposition was higher by 20 °C. Also, the endothermic transition was much smaller for the aged sample. The aged sample showed a crystalline melt transition around 40 °C which was not present in the original polymer. Attempts to anneal the polymer above the melt temperature and then quench to obtain an amorphous sample still did not result in the initially observed decomposition behavior.

Several small-molecule compounds containing dichloroethylidene groups were investigated using STA (Figure 3.4). Bisphenol C (**II**) had a sharp exothermic peak at 267 °C which also corresponded to the peak in the mass loss rate. The significantly lower temperature of the exothermic decomposition may be due to the phenolic hydrogens in the molecule. Another small molecule, 2,2-bis(4-chlorophenyl)-1,1-dichloroethylene (DDE), showed no exothermic decomposition but rather an endothermic vaporization with complete weight loss. The diphenyl ester of bisphenol C (**V**) showed an initial endothermic vaporization followed by a small broad exotherm.





**Figure 3.3** Simultaneous-TGA/DSC results for bisphenol C-sebacoyl polyester (poly-5). (Original polymer).



**Figure 3.4** Small-molecule compounds containing the dichloroethyldene moiety.

The onset of weight loss is 335 °C, which is about 100 °C lower than where the exothermic reaction takes place for the corresponding bisphenol C polyarylate, poly-2.

As mentioned above it is also possible to determine an instantaneous heat of decomposition. This takes into account the simultaneous mass loss that is occurring. The heat generated (or absorbed) as the sample decomposes is associated with less mass. One way to determine instantaneous heats is to divide the heat flow curve by the actual mass at each point and then integrate the new area of the peak. (This is the method used in the RSI Orchestrator software accompanying the Rheometrics STA 1500.) This method only gives reasonable results for samples that have large transitions with small mass losses. The instantaneous heat must be greater than the heat based on the initial mass. For samples that had small transitions with mass loss it was found the calculated instantaneous heat of decomposition was less than that which was based on the initial

mass which is impossible. As the mass decreases the heat flow curve rises rapidly when dividing by the mass and therefore it is no longer possible to find a baseline. A better method is to determine the area at each time interval ( $\Delta t$ ) and then normalize that area with respect to the mass at that time. The normalized areas can then be summed to give the instantaneous heat of decomposition,  $\Delta H_{inst}$ , using the following approximation

$$\Delta H_{inst} = \int_{t_i}^{t_f} \frac{h(t)}{m(t)} dt \cong \sum_{i=i}^{i=f} \left[ \frac{\left( \frac{h_i + h_{i+1}}{2} \right) * \Delta t}{(m_i + m_{i+1}) / 2} \right] \quad (3.1)$$

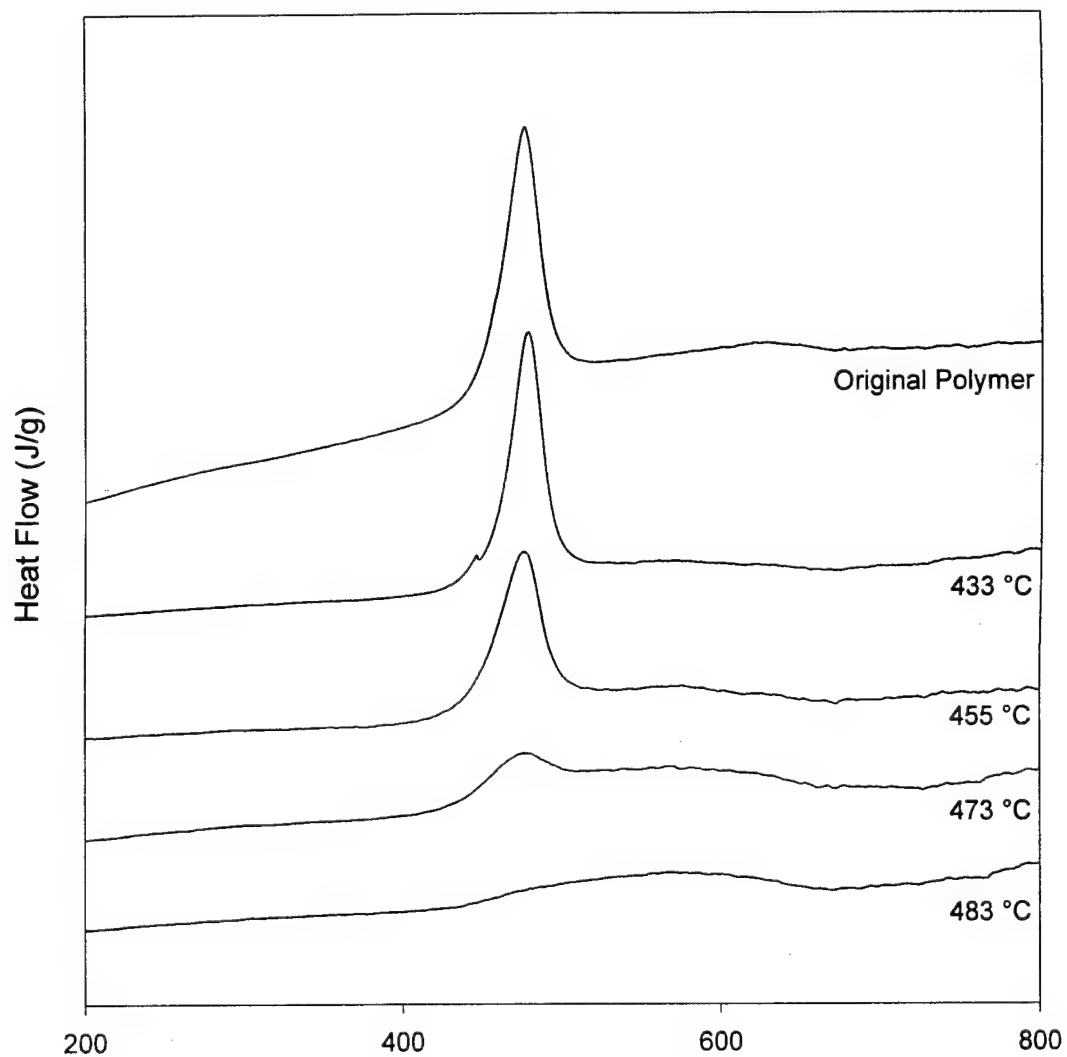
where  $h(t)$  and  $m(t)$  are the heat flow and mass at time,  $t$ , respectively. This method uses the original baseline and areas that were calculated for the heat of decomposition but then divides by the instantaneous mass.

The instantaneous heat of decomposition for poly-1 and poly-2 were determined to be 465 J/g and 430 J/g, respectively. The instantaneous heat of decomposition for these two polymers is 1.3-1.6 times greater the heat of decomposition based on the initial mass. The difference between the values gives some correlation between the mass loss associated with the heat of decomposition. The closer the two values the less mass that was lost during a particular decomposition. For samples that have zero or near zero char yields the differences will be much greater. For example, polyethylene was found to have an endothermic heat of decomposition around 250 to 350 J/g but the instantaneous heat of decomposition was found to be 830-850 J/g. The instantaneous heat of decomposition varies greatly depending on the limits of integration because the mass of the sample is

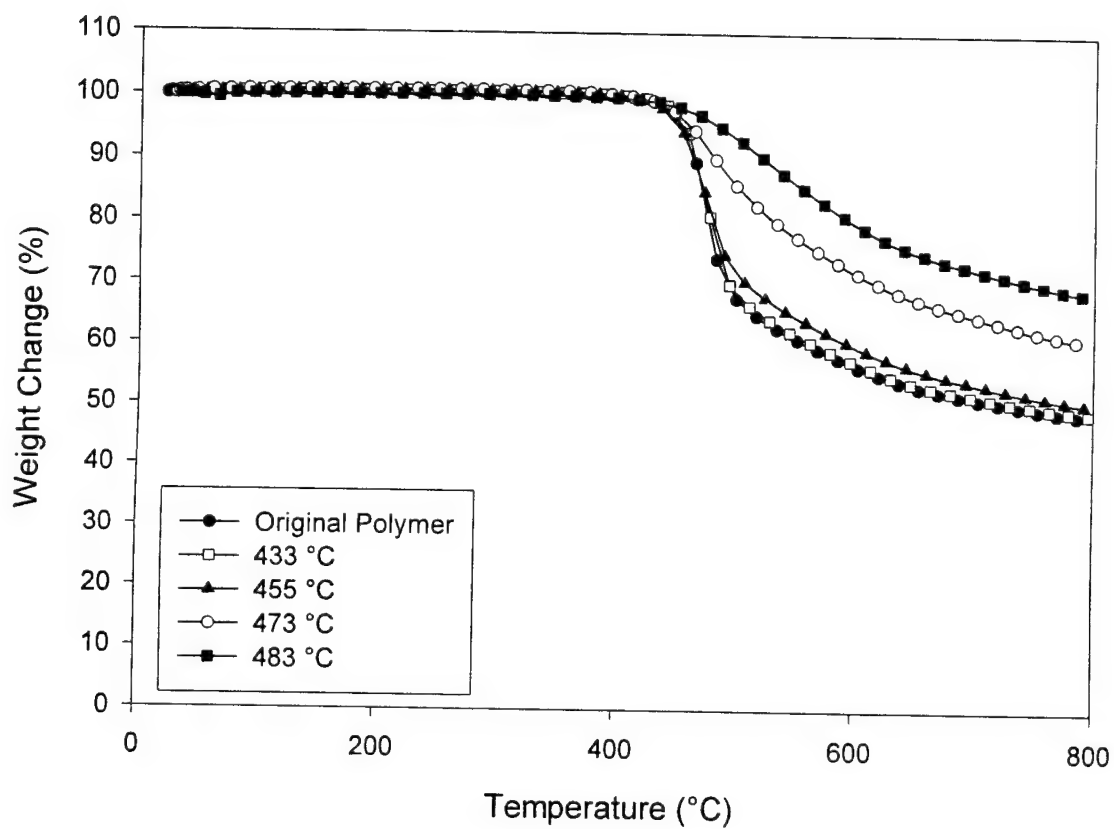
approaching zero and therefore the instantaneous heat of decomposition approaches infinity. This method of analysis is better suited for studying the instantaneous properties of the material remaining in the pan rather than integrating over a large range to access total heats.

An attempt to study the decomposition as a function of conversion was done by heating the polymer to a certain temperature at 10 °C/min in a TGA and then removing the sample immediately to stop the degradation. Samples were taken at 433, 455, 473 and 483 °C and then thermal analysis of the chars was performed using STA. The DSC curves from STA show that the decomposition is essentially unchanged (Figure 3.5). The samples all have an exothermic decomposition that occurs over the same temperature range. The char from 483 °C did not have the initially sharp exothermic peak but still had a broad exotherm over the entire range. The heat of decomposition was determined from each DSC curve and was normalized to the weight of the original sample. The remaining heat of decomposition is based on the partial areas from the DSC curve of the original polymer. A comparison of the values is shown in Table 3.3. As can be seen, the values do not match, with the actual measured heat of decomposition always being lower. This may be due to the fact that the reaction may still be going on between the time when the furnace stops heating and before the sample is removed to air. As the temperature at which the sample was taken increases, the difference between the measured and calculated heats becomes smaller. The onset of decomposition of each of char samples was about same (Figure 3.6).

Thermal analysis techniques can be used to determine kinetic data of decomposition reactions.<sup>8</sup> Reaction rate parameters can be determined using two



**Figure 3.5** DSC results from STA experiments for partially decomposed samples of bisphenol C polycarbonate. Samples were prepared by heating at 10 °C/min to final temperature and then removed to room temperature to halt further decomposition.



**Figure 3.6** TGA results for partially decomposed samples of bisphenol C polycarbonate. Samples were prepared by heating at 10 °C/min to final temperature and then removed to room temperature to halt further decomposition.

**Table 3.3** Decomposition behavior for bisphenol C polycarbonate as a function of the reaction conversion.

Sample	Char (%) <sup>a</sup>	Heat of Decomposition <sup>b</sup> (J/g)	Temperature at Peak of Exotherm (°C)	Temperature at Maximum Mass Loss Rate (°C)	Calculated Heat of Decomposition <sup>c</sup> (J/g)
Original	N/A	394	476	475	--
433 °C	99	322	478	475	383
455 °C	95	309	475	474	355
473 °C	83	248	475	475	256
483 °C	74	172	---	530	175

<sup>a</sup> Weight percent of the sample that was obtained as char. <sup>b</sup> Normalized with respect the weight of sample before any decomposition. <sup>c</sup> Heat of decomposition determined from partial area of the original polymer.

different methods: isothermal and non-isothermal. In order to calculate parameters under isothermal conditions the measurement at several different temperatures is required, whereas for non-isothermal methods the data can be calculated from one thermal analysis curve. A method proposed by Freeman and Carroll treats a single weight loss curve as one event, thereby determining the activation energy,  $E_a$ , pre-exponential factor,  $A$ , and the order of reaction, even though in many cases there are several processes going on during the decomposition of a polymer.<sup>9</sup> Here, the rate parameters were calculated assuming first order Arrhenius kinetics. The rate equation can be expressed as

$$\frac{d[X]}{dt} = -kf([X]) \quad (3.2)$$

where  $[X]$  is the concentration of reactant,  $f([X])$  is some function of  $[X]$  and  $k$  is the rate constant. The rate constant can be determined as a function of temperature,  $T$ , using the

Arrhenius equation

$$k = A \exp(-E_a / RT) \quad (3.3)$$

where R is the gas constant (8.314 kJ/mole). For TGA data, the rate constant at each temperature can be determined by dividing the mass loss rate (dm/dt) by the mass (m) at temperature, T. The slope of a plot of  $\ln k$  versus  $1/T$  is equal to  $-E_a/R$  and the y-intercept is equal to  $\ln A$ .

The kinetic rate parameters for several of the bisphenol based polymers were determined (Table 3.4). The bisphenol C polymers generally showed a wide temperature range at which the kinetic data follows a first order reaction rate. For the bisphenol C polycarbonate and polyarylates the activation energy is lower than the corresponding bisphenol A polymers.

**Table 3.4** Reaction rate parameters for various polymers calculated from TGA data.

Polymer	Activation Energy $E_a$ (kJ/mol)	Pre-Exponential Factor, $\ln A$	Temperature Range (°C)
poly-1	222	29.4	420-465
bisphenol A polycarbonate	322	43.6	469-521
poly-2	206	26.6	425-452
poly-3	343	48.4	467-510
poly-5	260	40.9	350-404
poly-6	227	32.8	374-445
poly-13	189	24.5	401-454

Determining rate parameters from DSC data can be more difficult due to fact that the curves can contain several peaks as was shown for the decomposition of BPA-PC. The bisphenol-C-containing polymers generally showed a single exothermic peak during



decomposition. Reaction rate parameters were calculated for poly-1 and poly-2 using Eq. 3.2 and 3.3. For the DSC data, the kinetic equation was written as a fraction of material reacted

$$\frac{d(H_T - H_t) / H_T}{dt} = -kt[(H_T - H_t) / H_T] \quad (3.4)$$

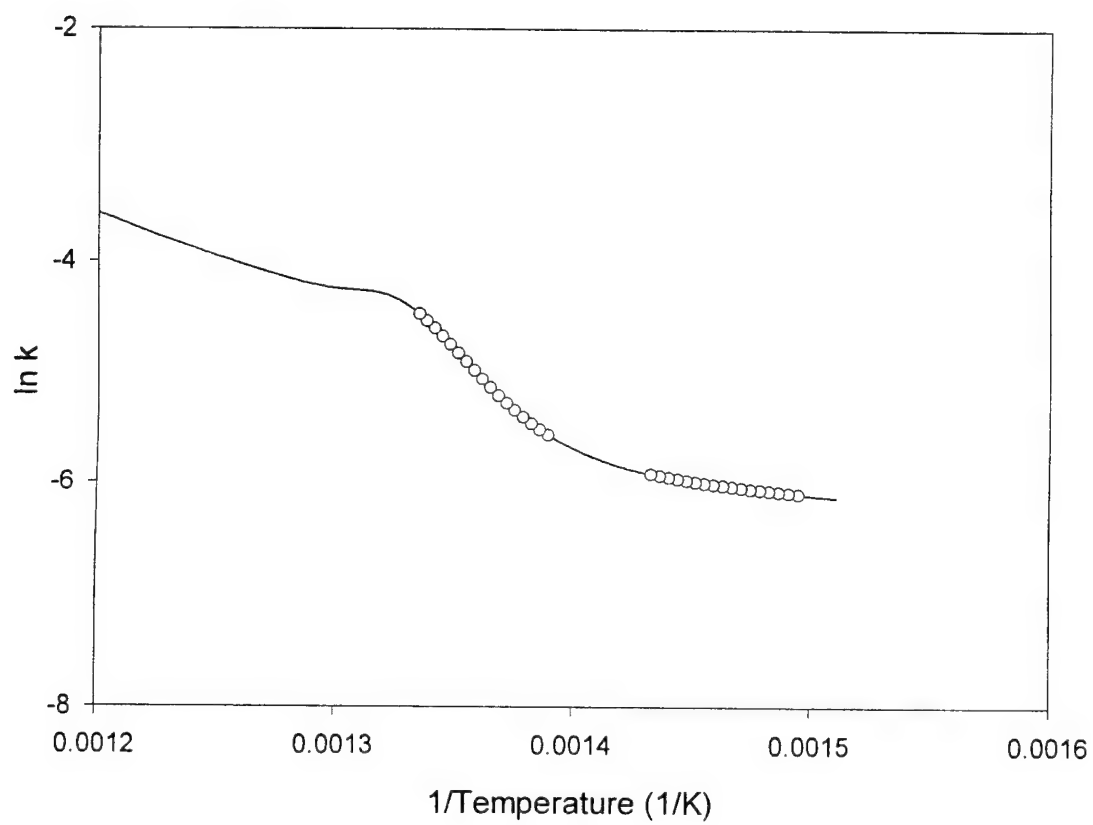
where  $H_T$  is the total heat of reaction and  $H_t$  is the heat of reaction up to time,  $t$ . The total heat of reaction,  $H_T$ , is a constant and  $d(H_T - H_t)/dt = -dH_t/dt$ ; therefore Eq. 3.4 can be rewritten as

$$\frac{dH_t}{dt} = kt(H_T - H_t) \quad (3.5)$$

The reaction parameters were determined using the first order Arrhenius equation. For both poly-1 and poly-2, there were two different events that showed first order behavior. Figure 3.7 shows a plot of the DSC kinetic data for poly-1. The first event was a low activation energy process with  $E_a$  equal to 34 kJ/mol and 28 kJ/mol for poly-1 and poly-2, respectively. The second region has an activation energy of 166 and 84.2 kJ/mol for poly-1 and poly-2, respectively.

#### 3.2.1.2 Spectroscopy

Various spectroscopic techniques were used to try to gain some insight into a decomposition mechanism for the bisphenol C materials. Infrared, Raman and X-ray photoelectron spectroscopy were all used and the results are described in this section.



**Figure 3.7** Kinetic plot of for DSC data for the decomposition of bisphenol C polycarbonate, poly-1.

Infrared spectroscopy was used to study the char at different stages in the decomposition. Solid samples were obtained using a TGA to heat the polymer to a desired temperature. IR spectra were obtained using an IR microscope with the sample being pressed between two diamond disks. The degraded samples obtained were all discolored, ranging from yellow to amber and then black. Peak assignments for the IR bands are shown in Table 3.5. The peak at  $974\text{ cm}^{-1}$  is attributed to the olefinic wagging

**Table 3.5** Infrared peak assignments for bisphenol C polycarbonate.

Peak	Assignment
1778	C=O stretch
1600, 1582, 1502, 1408	aromatic ring
1106-1261	C-O
1018	O-C-O stretch
974	C=Cl <sub>2</sub> wag
862	C-Cl stretch

of the =CCl<sub>2</sub> groups. Absent from the IR spectra is a band associated with the C=C olefinic stretching. For hydrocarbon substituted ethylenes, the C=C stretching frequency gives rise to bands in the range of  $1630\text{-}1680\text{ cm}^{-1}$ .<sup>10</sup> Replacing the hydrocarbon groups with chlorine usually lowers the frequency. While some of the C=C vibrations are weak in IR, they are usually strong in Raman. The Raman spectra for the same polycarbonate also does not have any distinct band that would be associated with the C=C stretching. Possibly the C=C stretching band occurs at the same frequency as the aromatic bands ( $1600$  and  $1583\text{ cm}^{-1}$ ).

From a qualitative comparison of the IR traces (Figure 3.8), there is little change in the polymer even after degradation at  $463\text{ }^{\circ}\text{C}$ . The most noticeable change is the broad

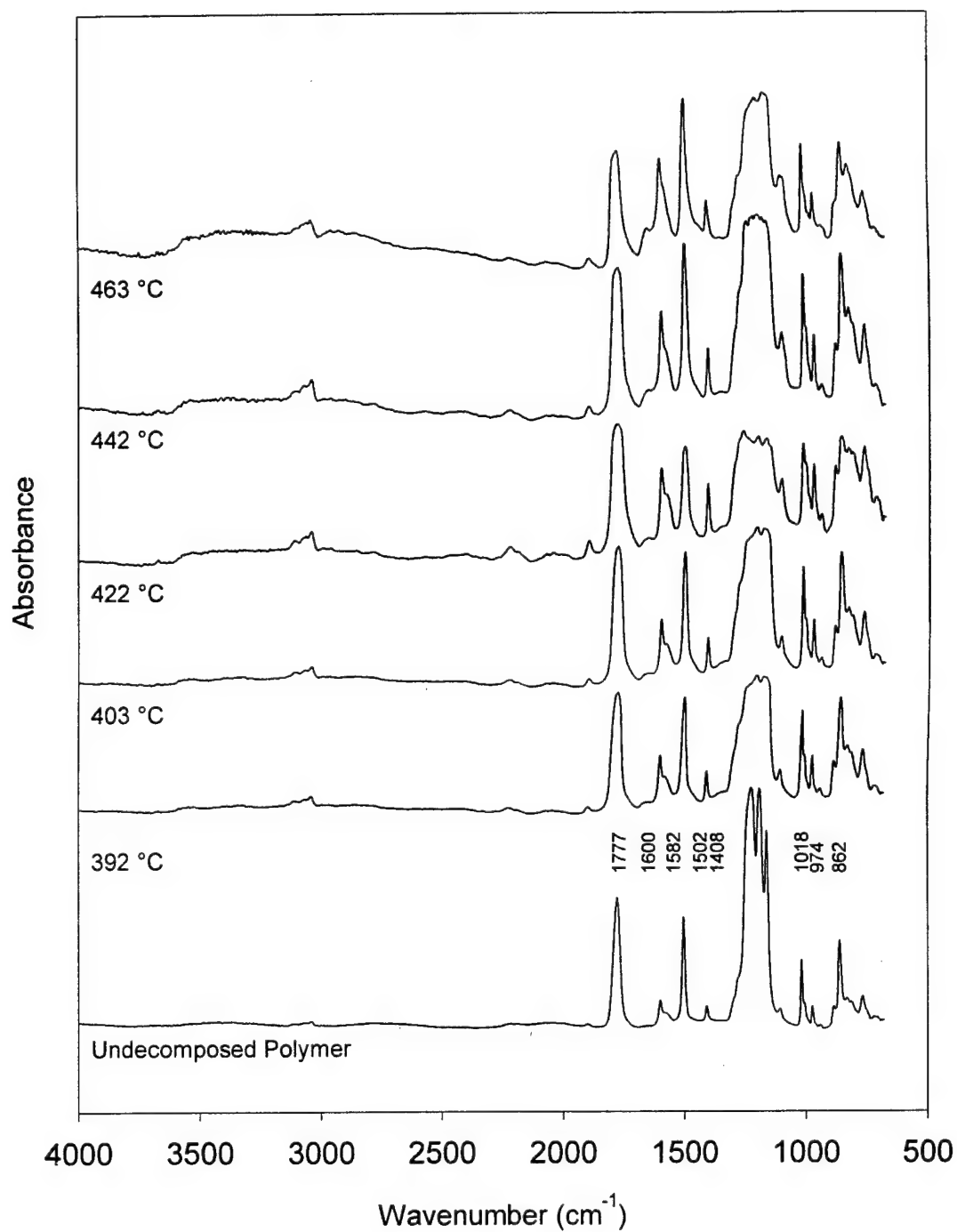
shoulder at  $1654\text{ cm}^{-1}$ . It is difficult to say much quantitatively because no one peak can be assumed to be constant. Most likely each of the bands is decreasing but at different rates. The band at  $1504\text{ cm}^{-1}$  was chosen to normalize all other bands. As can be seen from the data there is no clear trend in the data (Table 3.6). It appears that the intensity from bands associated with carbon-oxygen bonds have generally decreased when comparing data from the sample decomposed at  $463\text{ }^{\circ}\text{C}$  with the original polymer. Also, the intensity of the band at  $974\text{ cm}^{-1}$  has also decreased slightly. The data obtained for the sample exposed to  $403\text{ }^{\circ}\text{C}$  seems to lie outside the general trends.

**Table 3.6** Change in relative areas of Infrared bands a samples of bisphenol C polycarbonate decomposed at various temperatures. <sup>a</sup>

Band(s)	Original	392 $^{\circ}\text{C}$	403 $^{\circ}\text{C}$	422 $^{\circ}\text{C}$	442 $^{\circ}\text{C}$	463 $^{\circ}\text{C}$
1776	2.88	2.46	3.02	1.98	2.17	1.56
1600, 1582	0.38	0.57	0.89	0.60	0.65	0.69
1504	1.00	1.00	1.00	1.00	1.00	1.00
1408	0.10	0.14	0.23	0.15	0.19	0.12
1106-1261	13.95	7.64	6.11	6.62	6.67	5.38
1018	0.51	0.58	0.63	0.47	0.50	0.32
974	0.11	0.14	0.22	0.13	0.14	0.07

<sup>a</sup> Ratio of area of band to area of band at  $1504\text{ cm}^{-1}$ .

Raman spectroscopy is generally not used to investigate the decomposition behavior of polymers due to fluorescence. One exception has been the study of the degradation of poly(vinyl chloride).<sup>11</sup> The technique is extremely sensitive to the polyenes that are formed from the dehydrohalogenation of the polymer. We were interested in what changes were occurring in the polymer with degradation and in particular, what was happening with the dichloroethylidene group. Raman spectroscopy



**Figure 3.8** Infrared spectra of degraded bisphenol C polycarbonate samples exposed to different temperatures. The polymer was supplied by researchers at Federal Aviation Administration.

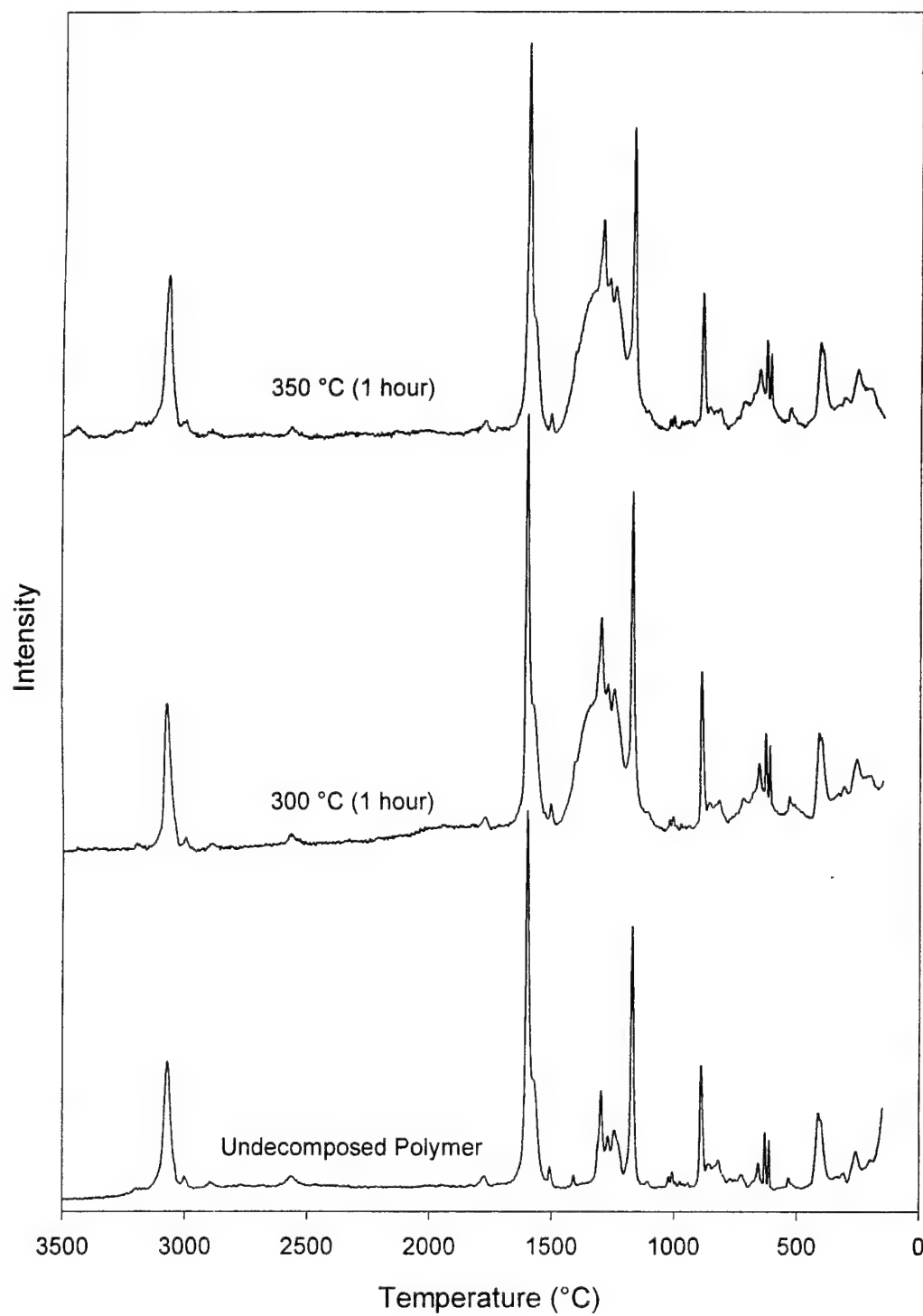
is generally more sensitive to ethylene vibrations giving rise to strong bands in the 1680-1570  $\text{cm}^{-1}$  range. Here samples were prepared by heating at various temperatures for 1 hour in a TGA furnace (Figure 3.9). For samples degraded at 300 °C and 350 °C, it was possible to obtain spectra even though the samples were discolored. (Spectra shown in Figure 3.9 for the degraded samples are baseline corrected). For the sample degraded at 400 °C, which was black, it was not possible to obtain any data since it appears that all of the light is absorbed. Very few changes occur in the spectra with the degraded samples. The biggest change is the large broad peak that appears around 1200-1400  $\text{cm}^{-1}$ .

Electron spectroscopy for chemical analysis (ESCA) is sensitive to the types of elements in a sample as well as the kinetic energy of the atoms.<sup>12</sup> Therefore, it is possible to distinguish atoms in different states. ESCA was used to study samples of degraded bisphenol C polycarbonate. Samples were solution cast onto quartz glass slides and then thoroughly dried under vacuum without heat. The polymers were then heated at a constant temperature for 1 hour in a tube furnace under a nitrogen atmosphere. Weight loss for the samples was not determined directly but samples were heated under the same conditions in TGA to give some indication of the amount of degradation (Table 3.7).

ESCA spectra were obtained at a take-off angle of 75° which corresponds to a sampling depth of 45 Å. A survey of elements of present in the control polymer

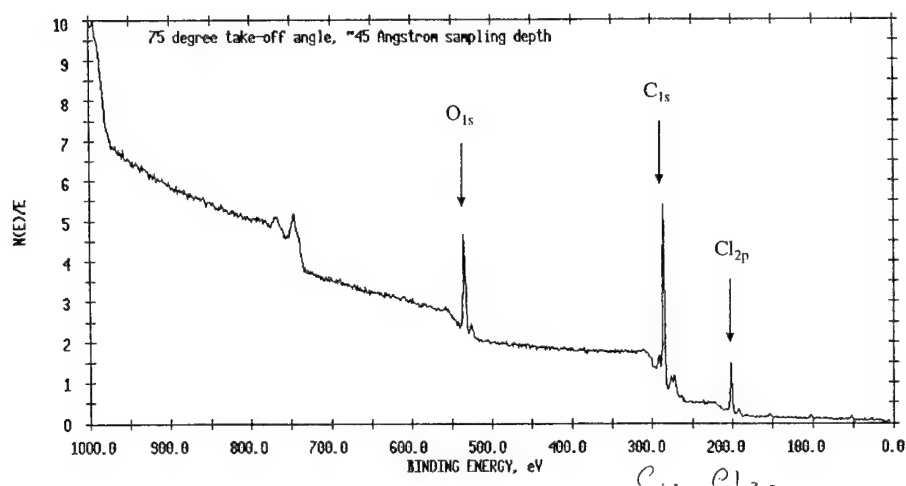
**Table 3.7** Corresponding weight loss for bisphenol C polycarbonate as determined by TGA for samples isothermally heated for 1 hour under nitrogen atmosphere.

Temperature (°C)	Weight Loss (%)
400°C	8
450°C	36
600°C	53



**Figure 3.9** Raman spectra of thermally decomposed bisphenol C polycarbonate. Samples were supplied by researchers at the Federal Aviation Administration.

(undecomposed sample) is shown in Figure 3.10. As expected the only elements present are oxygen, carbon and chlorine. ESCA multiplex spectra were taken in each of the regions of oxygen, carbon and chlorine for each of the samples. The percent of each element present is shown in Table 3.8. There is very little difference between the sample decomposed at 400 °C and the undecomposed sample although the decomposed sample is significantly discolored (brown-amber). The carbon to oxygen ratio stays the same ( $C/O = 5.0$ ) for the sample that was decomposed at 400°C. The amount of the chlorine for the original polymer is lower than that which was calculated. This difference may be due to some degradation of the sample by the X-ray beam. The original polymer was a clear film but after ESCA experiments the sample was slightly yellowed. It is difficult to make any conclusions on the change in chlorine at 400 °C but by 450 °C it is apparent



**Figure 3.10** Survey of elements for bisphenol C polycarbonate (undecomposed sample) from ESCA experiment. Polymer was supplied by researchers at the Federal Aviation Administration.



**Table 3.8** Chemical composition of degraded samples of bisphenol C polycarbonate as measured using ESCA compared with the microanalytical results.

		Carbon	Chlorine	Oxygen	C/Cl	C/O
Theoretical (calc)		75	10	15	7.5	5.0
ESCA	Control	76.62	7.95	15.44	9.6	5.0
	400 °C	76.27	8.93	14.80	8.5	5.1
	450 °C	85.15	2.03	12.83	42	6.6
	600 °C	90.99	0	9.01	---	10
Microanalytical	400 °C <sup>a</sup>	77.24	8.98	NA	8.6	---
	450 °C <sup>a</sup>	89.74	3.38	NA	26	---
	600 °C <sup>a</sup>	96.63	0	NA	---	---

<sup>a</sup> Degraded samples were prepared by heating in a TGA under nitrogen atmosphere.

that a significant portion of the chlorine is gone and by 600 °C there is no longer any chlorine present (at least that is detectable by ESCA).

The ESCA multiplex spectra for the carbon ( $C_{1s}$ ) region are shown in Figure 3.11. The carbon spectra remains unchanged for the sample decomposed at 400 °C when compared with the control sample. The large peak in the carbon multiplex shifts from 285.2 eV for the control sample to lower binding energy in the samples decomposed at 450 °C (284.5 eV) and 600 °C (284.2 eV), indicating possibly a more graphitic type structure is forming. The binding energy for carbon (graphite) is reported to be 284.2-284.3 eV in the literature.<sup>12</sup>

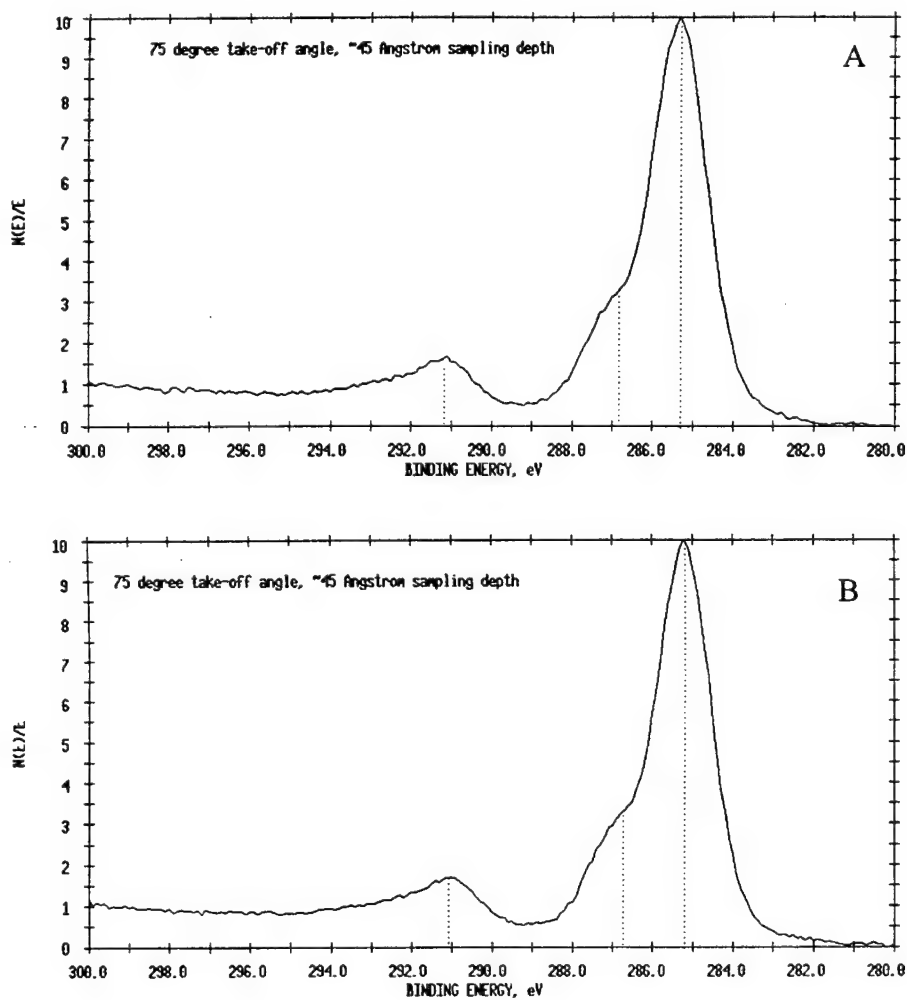
### 3.2.1.3 Pyrolysis GC/MS

In the previous section, the char remaining from the degraded polymer was studied. The use of IR, GC and MS with pyrolysis instrumentation allows for the analysis of the volatile products of polymer system during degradation. For typical polymers, the products observed in the gas phase are characteristic of the original polymer system.<sup>13</sup>

Identifying the products given off during decomposition can provide some insights into degradation routes of polymers and thermal stability profiles.<sup>14</sup>

In this research, polymers were pyrolyzed at 1200 °C at a heating rate of 10 °C/ms using a commercially available resistively heated filament pyrolyzer. The sample was pyrolyzed in a heated interface that was connected directly to the GC inlet. The pyrolysis products were swept directly onto the column where they were cold condensed. The GC oven was then ramped at 10 °C/min to 290 °C and the products were identified using a mass spectrometer. The mass range scanned ranged from  $m/z$  40 to 500. One concern to keep in mind when using a GC with a MS as the detector is that the area of the peaks (and height) is relative to amount of fragmentation in the molecule. For the data presented here, the results are discussed as relative areas. Therefore when comparing two spectra, the amount of a product is discussed as the peak area relative to another peak area. Unless otherwise noted, only peaks that were at least 1 % of the intensity of largest peak are considered.

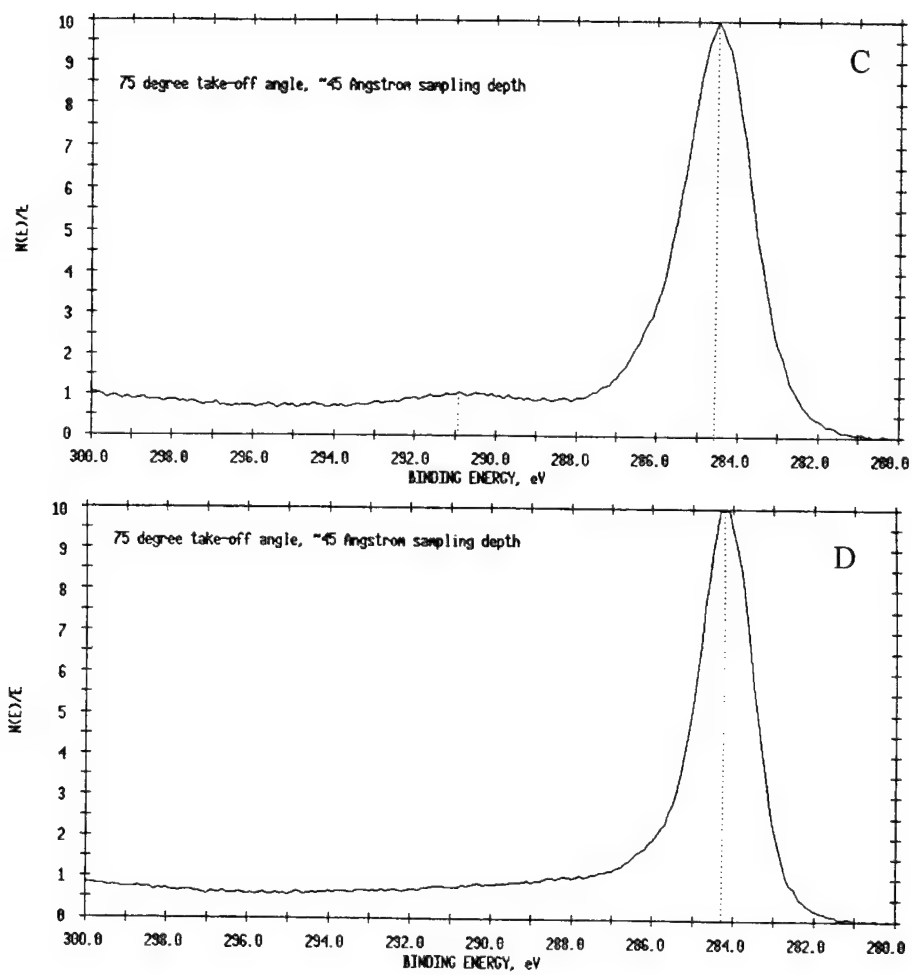
The GC trace from the pyrolysis of bisphenol C polyarylate is shown in Figure 3.12 along with the identification from the corresponding MS data. Since the mass spectra range was only to  $m/z$  40 the presence of HCl would not be detected. Other GC/MS data was obtained at lower  $m/z$  values of 34 but HCl was still not detected. This may be due to interaction of the generated HCl with the siloxane GC column. Pyrolysis gas-phase IR was done on a bisphenol C polycarbonate by Michael Ramirez at the FAA and shows the presence of HCl in the decomposition products along with large amounts of carbon dioxide (Figure 3.13). Analysis done at the FAA found that 80 to 90 % of the chlorine in the polymer is given off as HCl.<sup>15</sup> The presence of HCl does not show up in

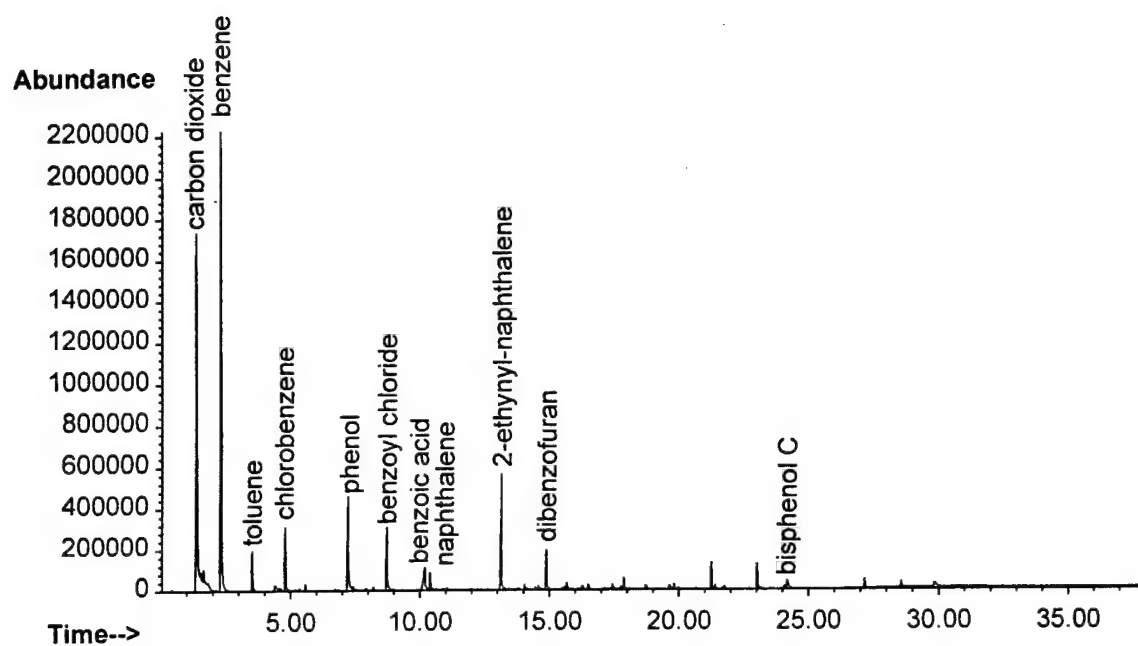


**Figure 3.11** Carbon (1s) region of ESCA spectra for bisphenol C polycarbonate. (A) undecomposed polymer, (B) decomposed at 400 °C for 1 hour, (C) decomposed at 450 °C for 1 hour, and (D) decomposed at 600 °C for 1 hour.

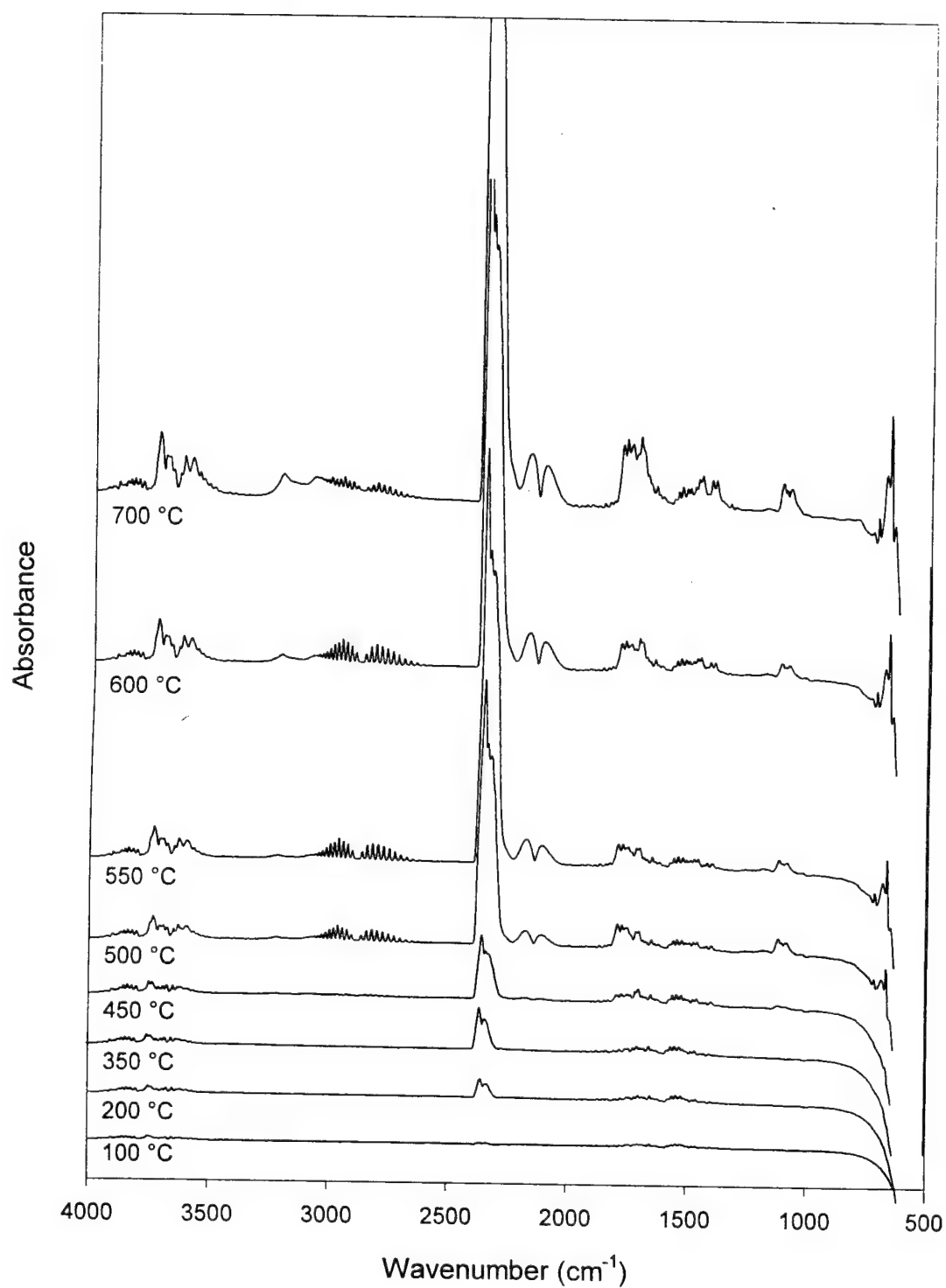
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Figure 3.11 continued





**Figure 3.12** GC trace of products from the pyrolysis of bisphenol C polyarylate, poly-2.



**Figure 3.13** Gas-phase Infrared spectra of decomposition products from bisphenol C polycarbonate. These spectra were obtained by Michael Ramirez at the Federal Aviation Administration.

the IR spectra until 500 °C whereas the presence of carbon dioxide starts appearing at 200 °C. The other major chlorinated products were identified by Py-GC/MS to be chlorobenzene and benzoyl chloride with a small amount of bisphenol C.

A comparison of the GC traces for the bisphenol C polyarylate (poly-2) with other bisphenol-A-based polyarylates, poly-3 and poly-8, shows that the bisphenol C polyarylate has fewer organic products when compared with the amount of carbon dioxide. Also, poly-2 has only a small amount of monomer generated during the pyrolysis whereas the two bisphenol A polyarylates generate significant amounts of monomer. The products from the bisphenol A polyarylates contain many substituted phenols (methyl, dimethyl, ethyl, isopropyl) whereas poly-2 does not yield significant amounts of substituted phenols. These trends were also observed for the bisphenol C polycarbonate and the bisphenol A polycarbonate (GC traces are shown in Appendix D).

Bisphenol C (II) and bisphenol C aliphatic polyesters (poly-4 and poly-5) all yielded significant amounts of bisphenol C during their degradation. The large amounts of undecomposed product from the pyrolysis of II was surprising, considering the large exotherm and char yield found from simultaneous-TGA/DSC. The reason for the presence of undecomposed sample may be due to the much more rapid heating rate used for the pyrolysis-GC/MS experiments. The presence of greater amounts of bisphenol C from the aliphatic polyesters when compared with the polyarylates may be due to the lower degradation temperatures of the polyesters. The decomposition of the backbone bonds may occur at a sufficiently lower temperature to allow the release of bisphenol C before it has a chance to undergo any reaction.

Pyrolysis-GC/MS was also performed on one of the charred samples (463 °C). The GC trace shows many of the same compounds as from the original polymer except chloro-substituted phenols (2-chlorophenol, 1,3-dichlorophenol, 2,4-dichlorophenol, *p*-chlorophenol) constitute a greater percentage of the decomposition products.

Pyrolysis-GC/MS of poly-**13**, the bisphenol C brominated polyarylate, mainly contained halogenated benzenes (chloro-, bromo-, dichloro, bromo-dichloro-, bromo-trichloro, dibromo, tribromo-benzene). Benzene was not a major product in of the decomposition of poly-**13**. This indicates that the benzene generated from poly-**2**, is probably due mainly to the terephthaloyl and isophthaloyl groups rather than to decomposition of the bisphenol C group. This polymer also did not yield significant amounts of the monomer, bisphenol C, during decomposition.

### **3.2.2 Blends and Copolymers**

#### **3.2.2.1 Thermal Analysis**

A series of copolymers, with varying amounts of bisphenol C and bisphenol A, were studied using STA. The results are summarized in Table 3.9 and the TGA curves are shown in Figure 3.14. Blends of the two polyarylate homopolymers, poly-**2** and poly-**3**, were also prepared (Table 3.10 and Figure 3.15). For both the blends and copolymers the char yield increases with increasing amount of bisphenol C in the polymer system. The char yields are always greater than what would be expected from a purely additive effect (Figure 3.16). In general, blending up to 50 wt% bisphenol A polyarylate, poly-**3**, into the bisphenol C polyarylate, poly-**2**, has little effect on decreasing the char yield.



**Table 3.9** Summary of TGA results for polyarylate copolymers containing varying amounts of bisphenol A and bisphenol C.

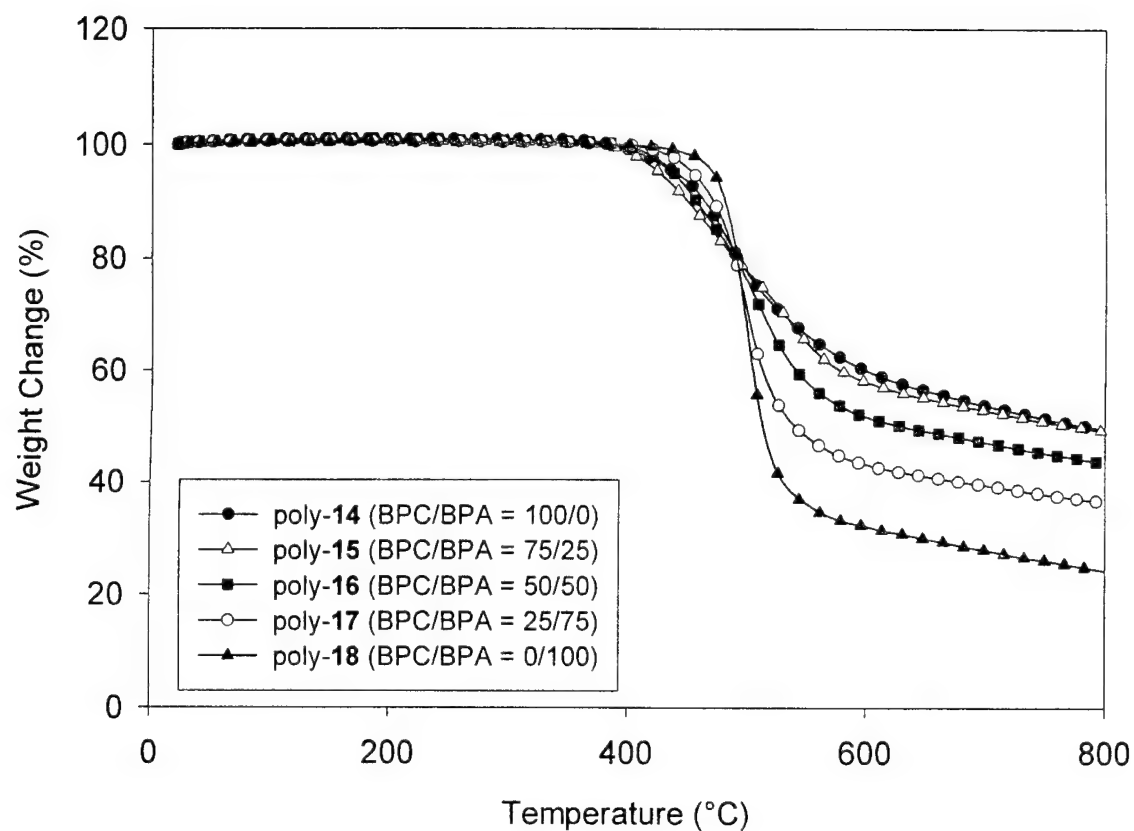
Sample	Fraction of BPC to BPA (wt %)	Onset of Decomposition (°C)	Char Yield at 700 °C (%)
poly-14	100	430 ± 5	52 ± 1
poly-15	77	432 ± 6	54 ± 0
poly-16	53	439 ± 5	47 ± 1
poly-17	28	457 ± 2	40 ± 0
poly-18	0	472 ± 1	29 ± 1

**Table 3.10** Summary of TGA results for polyarylate blends of bisphenol C polyarylate (poly-2) and bisphenol A polyarylate (poly-3).

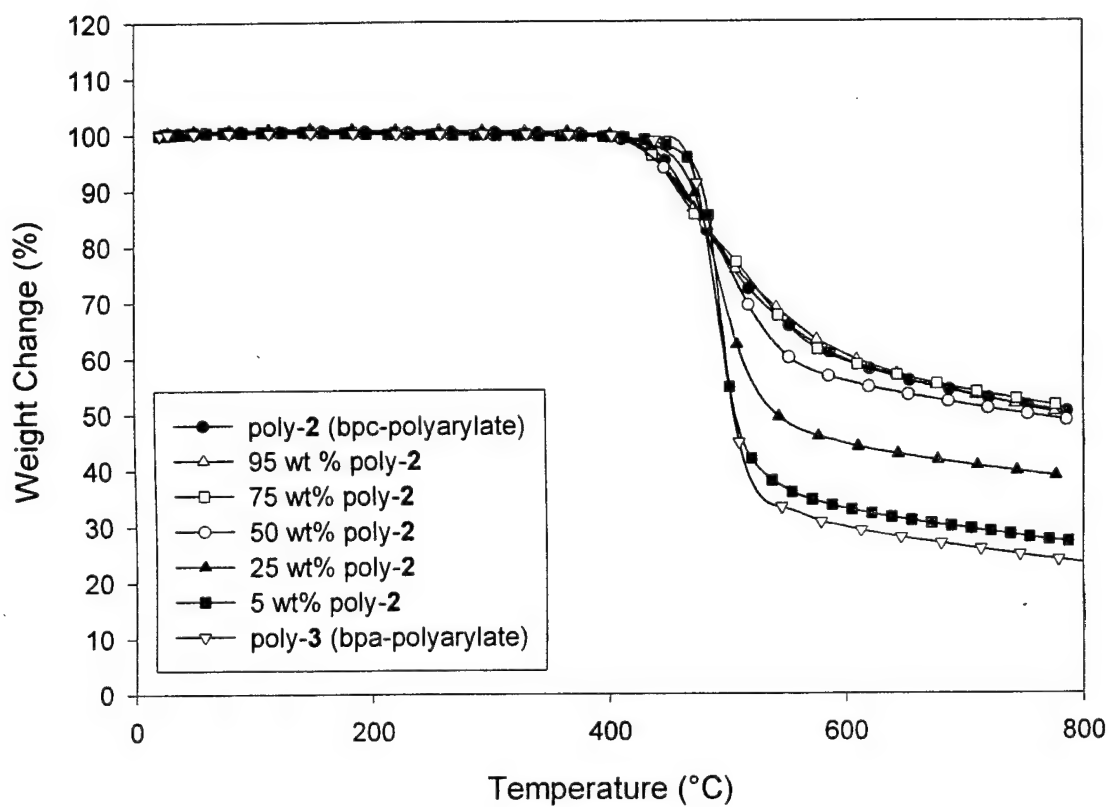
Sample (wt % of poly-2)	Onset of Decomposition (°C)	Char Yield at 700 °C (%)
100	455	53
95	446	54
75	442	54
50	445	53
25	455	41
5	470	30
0	469	27

Bisphenol C polyarylate, poly-2, was also blended with bisphenol A polycarbonate and bisphenol A polysulfone. Blends of poly-2 with polycarbonate showed similar behavior to that of the polyarylate blends (Table 3.11). The blends all had char yields greater than expected based on an additive effect. A sampling of the DSC thermograms are shown in Figure 3.17. Blends containing up to 20 wt% BPA-PC showed exothermic decomposition. Beyond this amount, the blends showed a combination of exothermic and endothermic reactions.

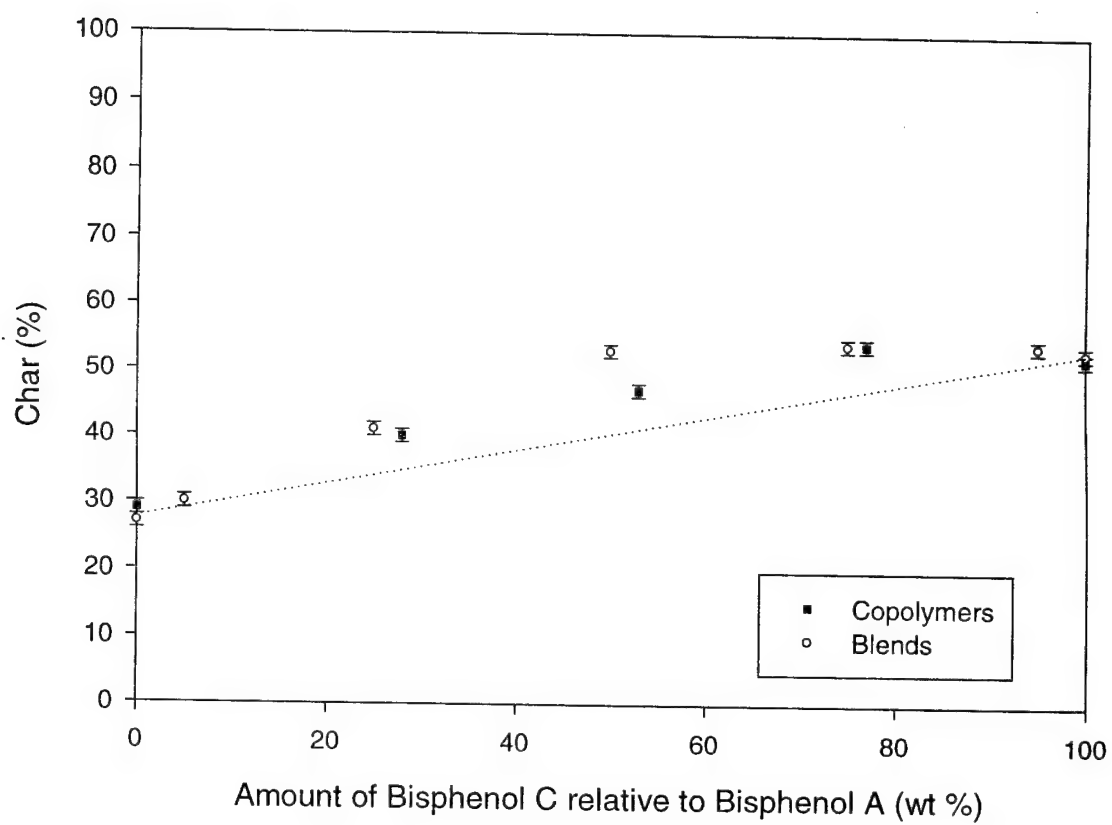
The blends with polysulfone showed the greatest char enhancement (Table 3.12). The char yield for blends containing only 25 wt% poly-2 had a char yield of 54 wt%



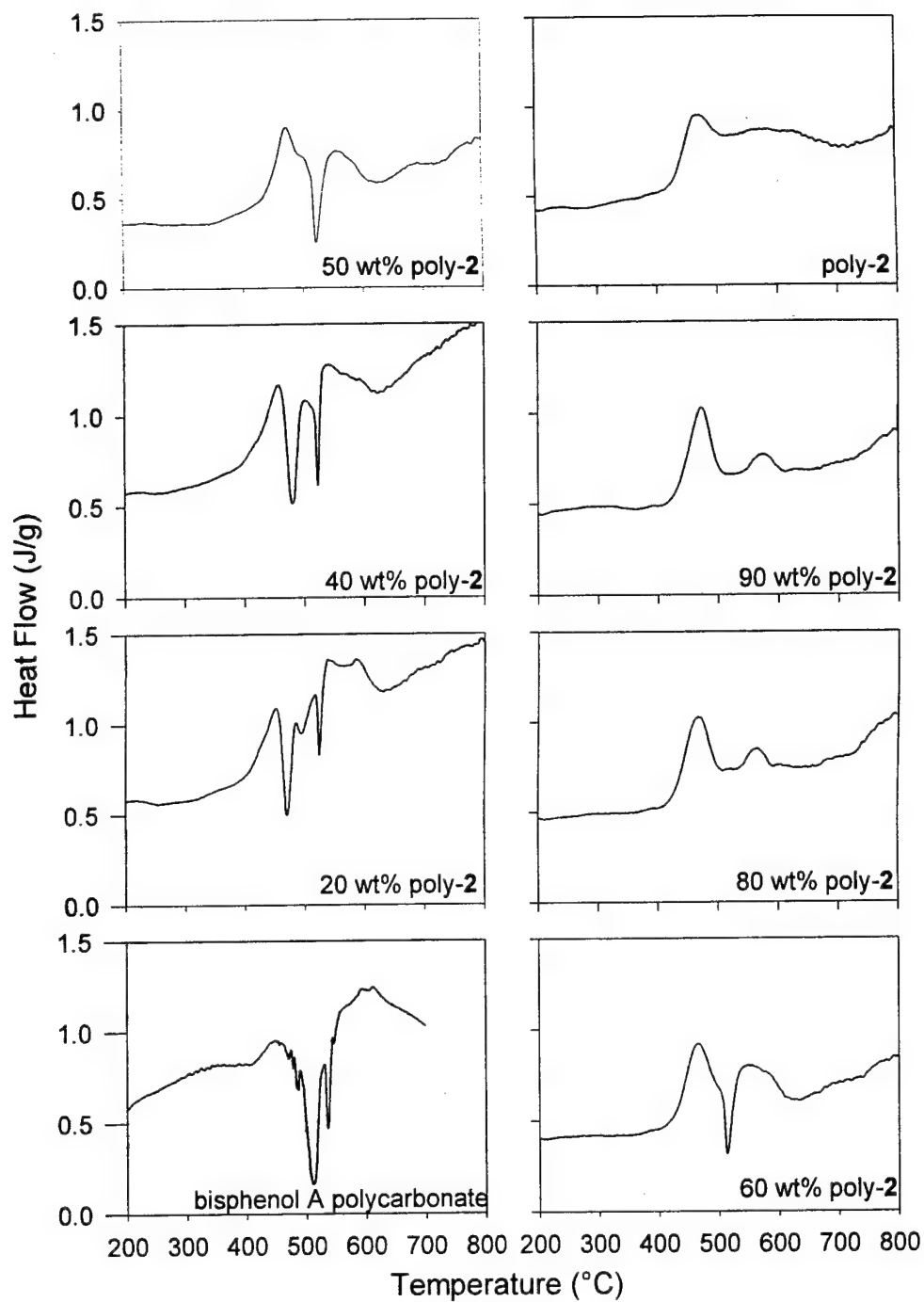
**Figure 3.14** TGA results for polyarylate copolymers containing varying amounts of bisphenol C and bisphenol A.



**Figure 3.15** TGA results for blends of bisphenol C polyarylate (poly-2) and bisphenol A polyarylate (poly-3).



**Figure 3.16** Comparison of char yields for polyarylate copolymers and blends.



**Figure 3.17** DSC thermograms from STA experiments of blends of bisphenol C polyarylate (poly-2) with bisphenol C polycarbonate.

**Table 3.11** TGA results for blends of bisphenol A polycarbonate with bisphenol C polyarylate (poly-2).

Sample	Onset of Decomposition (°C)	Char Yield at 700°C (%)
bisphenol A polycarbonate	454	19
20 wt% poly-2	452	31
40 wt% poly-2	446	40
50 wt% poly-2	257	46
60 wt% poly-2	447	51
70 wt% poly-2	447	53
80 wt% poly-2	445	54
90 wt% poly-2	450	55
poly-2	455	53

**Table 3.12** TGA results for blends of bisphenol A polysulfone and bisphenol C polyarylate (poly-2).

Sample	Onset of Decomposition (°C)	Char Yield at 700°C (%)
bisphenol A polysulfone	503	33
25 wt% poly-2	455	52
50 wt% poly-2	460	50
poly-2	455	53

BPC, **II**, or DPE-BPC, **V**, were also prepared. Adding these small molecules did not show any char enhancement (38 wt% calculated from additive effect). Blends of polysulfone with either 25 wt% of char enhancement for the polysulfone. The films from these blends were transparent and DSC traces did not show any melting transitions from the small molecules.

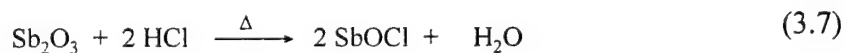
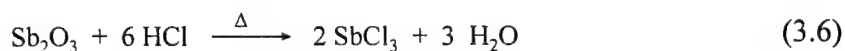
#### 3.2.2.2 Pyrolysis GC-MS

The degradation products of each of the copolymers and blends were determined using Py-GC/MS. The GC traces were generally a combination of the products identified from the corresponding homopolymers. The major peaks along with peak area as a

percent of the total area of all peaks are shown in Table 3.13. The relative yield of carbon dioxide decreases as the amount of bisphenol C polyarylate is decreased. One interesting observation is the generation of greater amounts of bisphenol C monomer for blends containing 75%, 50% and 25% of poly-2, relative to the homopolymer. The generation of more bisphenol C monomer was also observed for 50 wt% blends of poly-2 with bisphenol A polysulfone and bisphenol A polycarbonate.

### 3.2.3 Effect of Antimony Oxide

Antimony oxide has been known to have synergistic effects with halogenated flame retardants.<sup>16,17</sup> For halogenated materials that liberate HCl during decomposition the following equations have been proposed:



The decomposition behavior of bisphenol C polyarylate, poly-2, containing varying amounts of antimony oxide was studied using STA (Table 3.14 and Figure 3.18). For the sample with an Sb/Cl ratio of 1/3 the onset of decomposition was decreased by 70 °C. The decomposition was still exothermic in nature with a sharp exothermic peak followed by a broad shoulder. The antimony oxide containing samples all had a greater mass loss rate at the onset of weight loss. The char yields measured at 700 °C were about the same as that expected based on only the original mass of polymer. For the cases where less than a stoichiometric amount of antimony oxide was added, the samples showed a two

**Table 3.13** Products from the pyrolysis of bisphenol C polyarylate (poly-2), bisphenol A polyarylate (poly-3) and their blends along with yields calculated as a percent of the total area of all peaks.<sup>a</sup>

	Retention Time	poly-2	95	75	50	25	5	poly-3
CO <sub>2</sub>	1.36	28.9	25.0	15.8	10.1	9.2	7.5	10.6
benzene	2.31	33.7	37.0	35.3	27.8	26.3	23.4	25.5
toluene	3.53	2.3	2.8	4.9	6.4	7.5	8.3	7.6
chlorobenzene	4.80	3.3	2.8	1.2	---	---	---	NA
ethylbenzene	5.09	---	---	---	---	---	0.7	0.8
phenylethyne	5.38	---	---	---	---	---	0.6	0.9
styrene	5.61	0.4		0.7	1.3	1.4	2.1	2.8
phenol	7.25	5.6	7.4	11.4	13.5	13.6	12.0	14.3
benzoyl chloride	8.72	3.8	2.6	---	---	---	---	NA
4-methylphenol	8.77	---	---	2.4	5.3	7.7	6.1	4.4
benzoic acid	10.20	3.2	2.3	2.9	4.6	4.1	---	---
naphthalene	10.41	1.0	1.0	1.2	1.2	0.9	---	1.6
2-ethynyl naphthalene	13.13	5.7	6.5	7.8	7.3	6.9	6.3	6.4
acetanaphthalene	14.05	---	---	---	1.7	---	---	2.1
dibenzofuran	14.87	2.4	2.9	4.0	4.1	---	3.7	3.8
4-cumylphenol & bisphenol A	21.65	NA	---	---	2.1	3.0	5.7	4.1
bisphenol C	24.19	1.0	--	4.2	6.4	3.3	---	NA

<sup>a</sup> Columns may not add up to 100 % due to the fact that not all peaks are shown in the table.

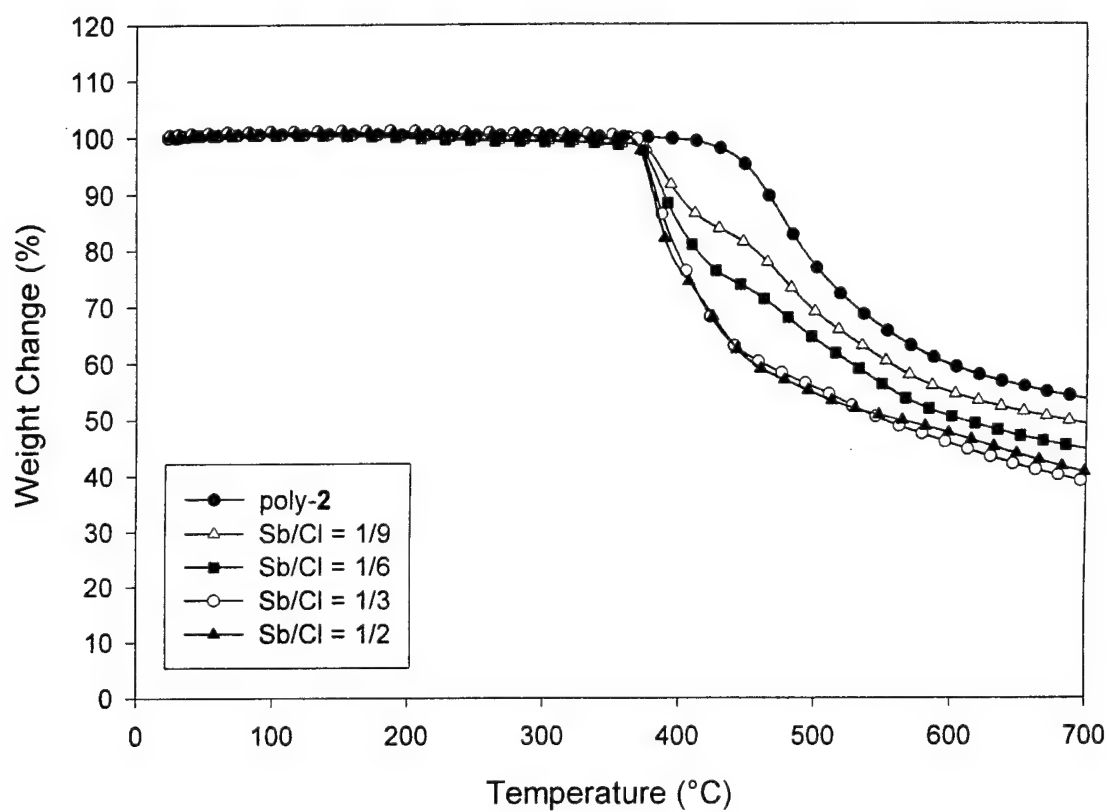
**Table 3.14** Summary of TGA results for antimony oxide in bisphenol C polyarylate (poly-2).<sup>a</sup>

Weight Percent of Antimony Oxide in Poly-2 (wt %)	Sb/Cl	Onset of Decomposition (°C)	Char Yield at 700 °C (%)	Char Yield Based on Initial Mass of Polymer (%)
0	0	455	52	52
7.2	1/9	385	49	53
10	1/6	381	45	50
20	1/3	378	38	55
26	1/2	376	40	48

<sup>a</sup> Columns may not add up to 100 % due to the fact that not all peaks are shown in the table.

step decomposition with the second step occurring at the same temperature as the pure polymer. Antimony oxide has an endothermic weight loss peak at 655 °C due to





**Figure 3.18** TGA results for antimony oxide in bisphenol C polyarylate (poly-2).

sublimation which was not present in the DSC traces of any of antimony-containing polyarylate samples.

Further investigation of the antimony oxide in poly-2 was done using Py-GC/MS. The amount of carbon dioxide generated is greater for the sample containing antimony oxide (Table 3.15). The decomposition products also no longer include benzoic acid and benzoyl chloride. These results indicated that perhaps the antimony oxide was causing the degradation of the polyarylate prematurely due to a interaction with the ester group. A sample of bisphenol A polyarylate (poly-3) was then prepared containing 20 wt% antimony oxide. This polymer also had an earlier onset of decomposition by about 70 °C. The DSC trace from STA, showed an endothermic peak due to remaining unreacted antimony oxide.

**Table 3.15** Comparison of product yields for antimony oxide containing bisphenol C polyarylate (poly-2).

Product	Retention Time	poly-2	poly-2 with 20 wt% Sb <sub>2</sub> O <sub>3</sub>
CO <sub>2</sub>	1.36	28.9	44.5
benzene	2.30	33.7	32.5
toluene	3.53	2.3	1.9
chlorobenzene	4.80	3.3	3.3
styrene	5.58	0.5	0.5
phenol	7.21	5.6	2.3
benzoyl chloride	8.72	3.8	---
benzoic acid	10.20	3.2	---
naphthalene	10.41	1.0	1.3
2-ethynylnaphthalene	13.13	5.7	4.8
dibenzofuran	14.88	2.4	2.1
bisphenol C	24.19	1.0	---

### **3.3 Combustion properties of polymers**

#### **3.3.1 Introduction**

There are many tests for measuring the combustion properties of polymers, although there is no universal method for determining the fire performance of a material. There are three main categories of tests for the combustion of materials: small-, medium- and large-scale tests. Of course large scale tests are the most realistic and give the best representation of full-scale fires but are impractical from the view of expense and are difficult to replicate. Medium-scale tests can be designed to give information that correlates well with full-scale tests. These tests allow for a quantitative measure of the materials' flammability properties and can be performed at varying heat fluxes which leads to more realistic conditions that the material will see. Small-scale tests are by far the most practical for screening materials, especially new materials where amounts may be scarce. The problems with testing of materials in small-scale tests include making measurements at one heat flux and assuming that they are linear over the range. This is not the case for most materials. Therefore, it is necessary to know what the fire properties of a particular material are at actual large fire conditions, but without doing a large scale test.

#### **3.3.2 Methods of Determining Combustion Properties**

The most often used test to evaluate a polymer as a fire hazard has been the Limiting Oxygen Index (LOI).<sup>18</sup> Some representative LOI values for polymers are shown in Table 3.16. LOI values for dichloroethylidene containing polymers is shown in Table 3.17 for comparison. This method measures the amount of oxygen (percent)

**Table 3.16** Limiting Oxygen Index (LOI) values for various commercially available polymers.<sup>19-21</sup>

Polymer	Limiting Oxygen Index (LOI)
Polyoxymethylene	15.7
Polyethylene	17.4
Polypropylene	17.4
Polystyrene	17.6-18.3
Polymethylmethacrylate	17.4
Polycarbonate	26-28
Polyethyleneterephthalate	20
Bisphenol A polysulfone	30
Polyethersulfone	37-42
Polyetheretherketone	35
Polyarylsulfone	38
Polybenzimidazole	41
Polyvinylchloride	45-49
Polyetherimide	47
Polytetrafluoroethylene	95

**Table 3.17** Limiting Oxygen Index (LOI) values for polymers containing dichloroethylidene moiety ( $C=CCl_2$ ).<sup>23,24</sup>

Polymer	Limiting Oxygen Index (LOI)
Polycarbonate	56
Polyarylate	46
Brominated polyarylate	60
Aromatic polyamide	57-60
Polyimide	37
Chlorinated polyimide	63

needed to sustain combustion. The higher the LOI, the better the material is with respect to flammability. This test is convenient and easily reproducible. LOI values correlate well with other flammability parameters.<sup>22</sup> The problem with LOI tests is that there is an unrealistically high concentration of oxygen and therefore it does not correlate well with performance under actual fire conditions.

LOI is only applicable to study the combustion behavior at ambient temperature.<sup>25</sup> In a real fire the material is typically at a much higher temperature when it catches fire. When the LOI is measured as a function of temperature, all of the LOI values decrease with increasing temperature. Values for pure polymers decrease gradually with temperature whereas polymers containing additive-type flame retardants decrease slowly to a certain temperature but then rapidly drop off as the flame retardant volatilizes or decomposes.

Heat release rate is one of the most important parameters in determining a material's potential fire hazard.<sup>26</sup> The smaller the heat release rate, the less the material contributes towards sustaining combustion. There are several tests for measuring this parameter, including the Factory Mutual calorimeter test, the Ohio State University (OSU) release rate apparatus and the cone calorimeter. Cone calorimetry calculates the heat release rate based on the oxygen consumption method.<sup>27</sup> Using Thornton's rule

$$\dot{q} = E(\dot{m}_{O_2}^\circ - \dot{m}_{O_2}) \quad (3.8)$$

the heat release rate,  $\dot{q}$ , can be calculated based on the rate of oxygen consumed, where  $E$  is equal to 13.1 kJ/g  $O_2$  for most polymers. The OSU heat release apparatus measures the actual heat released from combustion by measuring the temperature of the exhaust gases.<sup>28</sup> The Factory Mutual calorimeter allows for the measurement of flame spread as well as heat release and smoke generation. These types of tests are used extensively by the FAA and measured specifications and ratings are established using these methods.

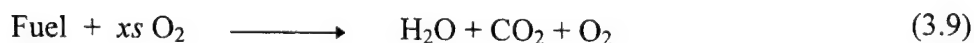
One other test that is commonly referred to in the literature is the UL-94 vertical flame test. This test has been described in detail along with specifications for

classification.<sup>29</sup> This test applies a Bunsen burner flame to a specimen for ten-second exposure intervals. Usually five specimens are used with two ten-second intervals. If none of the specimens sustain a flame for longer than ten seconds after removal of the Bunsen burner, the material gets a V-0 rating. If none of the specimens sustain burning for longer than 30 seconds, then the materials gets a V-1 rating. A V-2 rating is the same as a V-1 rating except that the burning polymer drips and a cotton specimen, located below the sample, ignites.

### 3.3.3 Microcalorimetry

A pyrolysis-combustion flow calorimeter (PCFC) was developed by researchers at the FAA that allows for the measurement of combustion properties using only milligram quantities of sample. Other tests, such as the cone calorimeter require about 100 grams for one test whereas each test on in the PCFC requires only one milligram, therefore allowing for several replications with only small amounts of material being required. It is an ideal technique for measuring combustion properties of newly synthesized materials.

The basis of the test is that the material is pyrolyzed at high temperatures under a nitrogen atmosphere. The pyrolysis gases are swept into a furnace where they are combined with enough oxygen to completely react all gases as shown in following equation.



The carbon dioxide and water are scrubbed out of the exhaust and the amount of oxygen remaining is measured. The amount of oxygen is measured before and after the polymer is pyrolyzed (Figure 3.19). The peak heat release rate is determined using Thornton's Rule (Eq 3.8). The peak heat release,  $\dot{q}$ , is normalized with respect to the heating rate,  $\beta$ , and the sample mass,  $m$ , to give the peak heat release capacity,

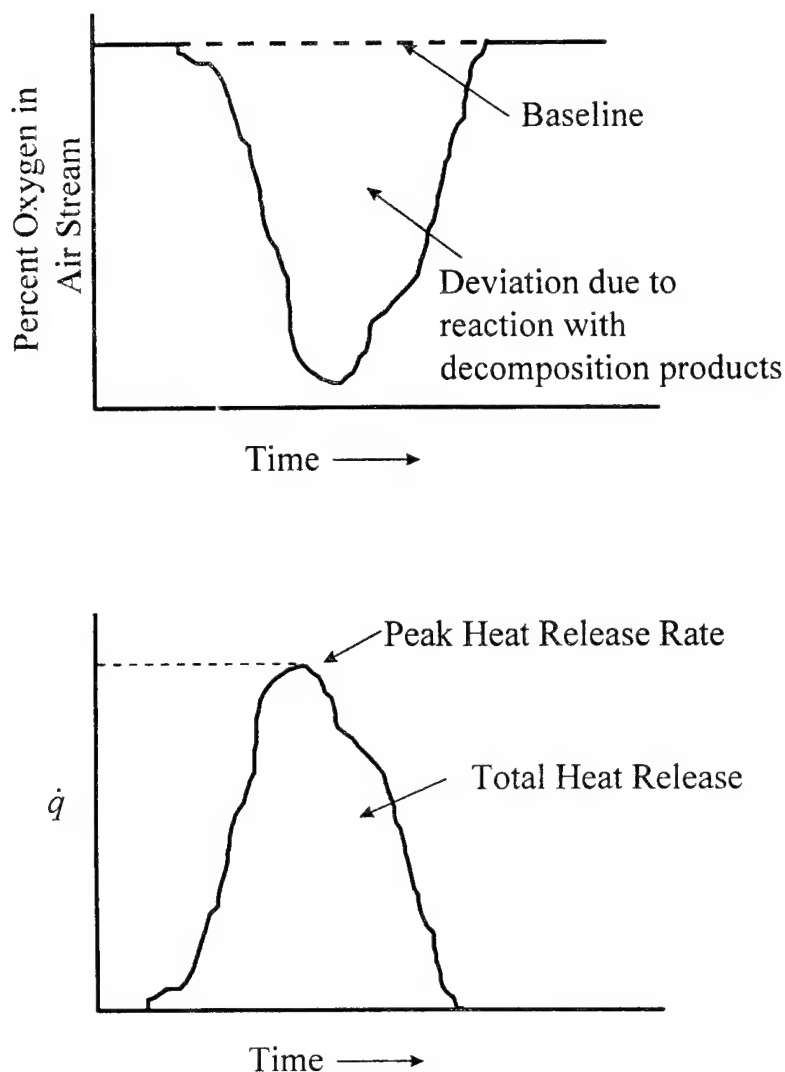
$$\eta_c = \frac{\dot{q}}{m\beta} \quad (3.10)$$

in units of J/g-K. The area under the heat release curve is integrated to give the total heat released during the decomposition.

The FAA has shown that results from these tests correlate well with the medium-scale tests, such as the cone calorimeter. Results have also been corroborated by researchers here at the University of Massachusetts-Amherst, where the amount and nature of the decomposition products were determined using a TGA coupled to a GC/MS.<sup>30,31</sup> By measuring the maximum rate of mass loss and calculating the heat of combustion of the products generated at this temperature, it was possible to determine the peak heat release capacity.

### 3.4 Results From Microcalorimetry

The combustion properties for the polymers described in Chapter 2 were measured using PCFC. Samples were heated at a rate of 4.3 °C/s from just below the decomposition temperature to 930 °C. Results are shown in Table 3.18. Bisphenol C polyarylates had some of the lowest peak heat release capacities measured. The blends



**Figure 3.19** Schematic of the method for determining the combustion properties from PCFC.

and copolymers of polyarylates were also measured by PCFC (Table 3.19). The results show similar trends to that of the enhanced char yields. Small amounts of bisphenol C polyarylate, poly-2, blended with bisphenol A polyarylate, poly-3, had the largest effect on reducing the peak heat release capacity (Figure 3.20). The addition of antimony oxide to poly-2 had a higher peak heat release capacity than the pure polymer. This can be attributed to the greater mass loss rate observed in the antimony oxide containing

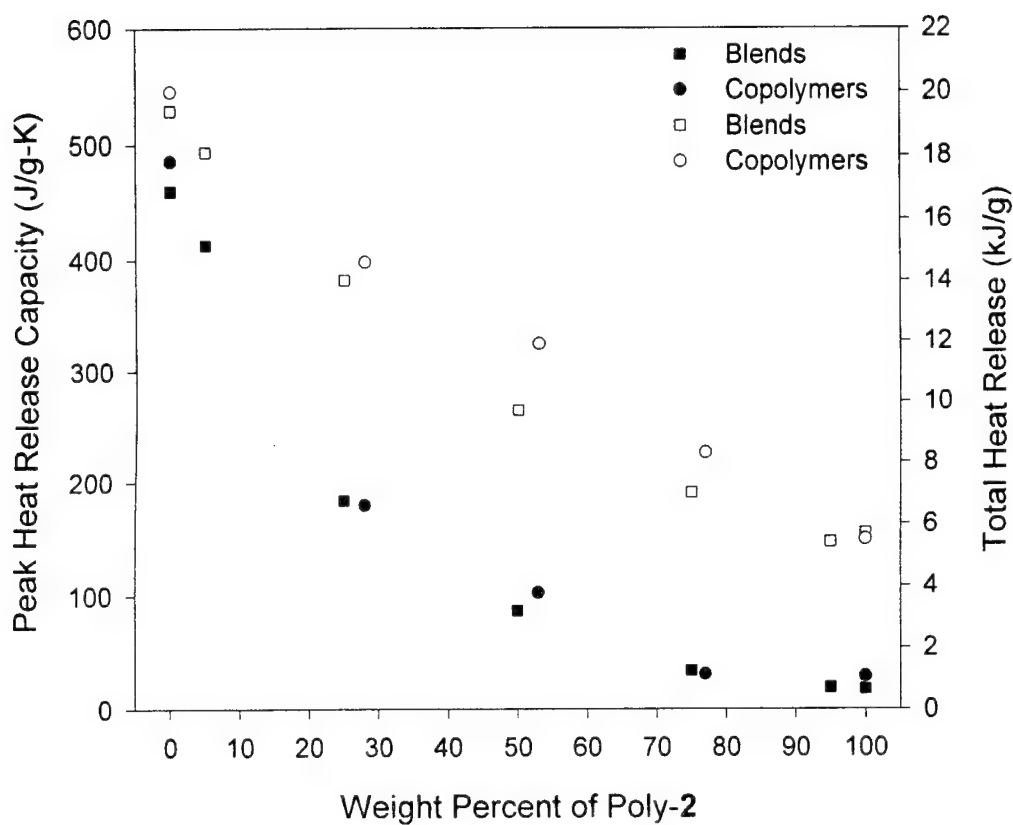


**Table 3.18** Results from PCFC experiments for bisphenol-C-containing materials and related polymers.

Sample	Peak Heat Release Capacity (J/g-K)	Total Heat Release (kJ/g)	Char Yield (%)
poly-6	706	35.7	0.3
poly-3	486	22.4	2.4
poly-5	251	19.2	47
DPE-BPC V	180	17.0	0
poly-10	158	14.7	39
BPC II	129	11.9	6
poly-8	124	7.7	38
poly-4	101	8.5	35
poly-9	83	6.2	32
poly-7	71	6.1	20
poly-1	51	7.4	49
poly-12	26	4.4	54
poly-13	26	3.5	35
poly-2	18	5.7	50
poly-11	18	6.3	47

polymer. For comparison, several values from PCFC are shown for commercial polymers (Table 3.20).

A nonlinear relationship of the combustion properties with bisphenol C content in the blends and copolymers was observed. Peak heat release capacity values for the blends and copolymers were much closer than the values for total heat release. Nonlinear results have been reported for limiting oxygen index (LOI) studies of polycarbonate blends.<sup>24</sup> Copolymers and blends prepared by compression molding all showed a linear relationship between the LOI value and the content of bisphenol C. The LOI values for blends prepared by injection molding showed a plateau for blends containing above 25 % bisphenol C polycarbonate.



**Figure 3.20** Peak heat release capacity and total heat release as a function of the weight percent of bisphenol C polyarylate, poly-2, in blends with bisphenol A polyarylate, poly-3. Solid symbols are peak heat release capacity values and open symbols are total heat release values.

**Table 3.19** PCFC results for blends, copolymers and additives.

Sample	Deconvoluted Heat Release Capacity (J/g-K)	Total Heat Released (kJ/g)	Char Yield (%)
poly-2	18	5.7	50
95/5	19	5.4	52
75/25	34	7.0	51
50/50	87	9.7	44
25/75	184	14.0	37
5/95	413	18.1	28
poly-3	460	19.4	25
poly-14	29	5.5	43
poly-15	31	8.3	50
poly-16	103	11.9	41
poly-17	175	14.6	36
poly-18	430	22.4	25
poly-2	18	5.7	50
50/50	69	25.8	42
bisphenol A polysulfone	327	16.3	28
poly-2	18	5.7	50
50/50	170	10.0	44
bisphenol A polycarbonate	390	21.2	21
poly-2 + 20 wt% Sb <sub>2</sub> O <sub>3</sub>	28	5.2	39

**Table 3.20** PCFC results for commercially available polymers.<sup>31</sup>

Polymer	Peak Heat Release Capacity (J/g-K)	Total Heat Release (kJ/g)	Char Yield (%)
Polyethylene	1560	42.7	0
Polypropylene	1313	44.3	0
Polystyrene	1040	39.2	0
Polyphenyleneoxide	458	20.8	24
Polycarbonate	390	21.2	21
Polyethyleneterephthalate	375	16.6	5
Polyethersulfone	228	15.3	29
Polyetheretherketone	155	12.4	47
Polyetherimide	121	11.8	49
Polyarylsulfone	115	13.5	43
Polyetherketoneketone	96	8.7	61

### 3.5 Discussion

Bisphenol C polymers have been shown to be some of the least combustible materials when studied using microcalorimetry. The exact reason for their exceptional flame resistance is not known but can be attributed to several factors, including low mass release rates, generation of noncombustible gases (HCl and CO<sub>2</sub>), and high char yields. One interesting observation for bisphenol C polymers that is contrary to that expected of materials that might be flame resistant is the exothermic decomposition reaction that takes place. It has been proposed that the design of materials that decompose in an endothermic fashion will help slow down combustion by acting as thermal sinks.<sup>32</sup> On the other hand, materials containing reactive groups, such as acetylene or BCBs, that undergo exothermic crosslinking reactions prior to decomposition, have been shown to have potential flame retardant applications because of their char enhancement.<sup>33,34</sup>

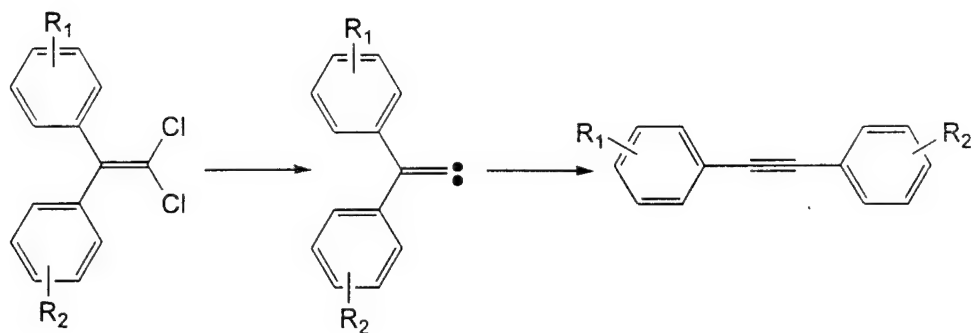
The mechanism for bisphenol C polymer decomposition is not known. The fact that the peak in mass loss rate occurs at the same temperature as the maximum in the exothermic peak indicates that the two processes may be related. One possible mechanism is that the loss of HCl leaves a highly reactive intermediate that undergoes an exothermic reaction. Another possible mechanism could be that an exothermic crosslinking reaction takes place through the double bonds generating enough heat to cause degradative weight loss.

While crosslinking through the double bonds has been suggested, it has not been discussed in the context of occurring during the thermal decomposition.<sup>2,3</sup> Crosslinking was reported for bisphenol C polycarbonate for samples that were heated for 4-8 hours at 200-240 °C in air based on the fact that they became insoluble. The polymers were

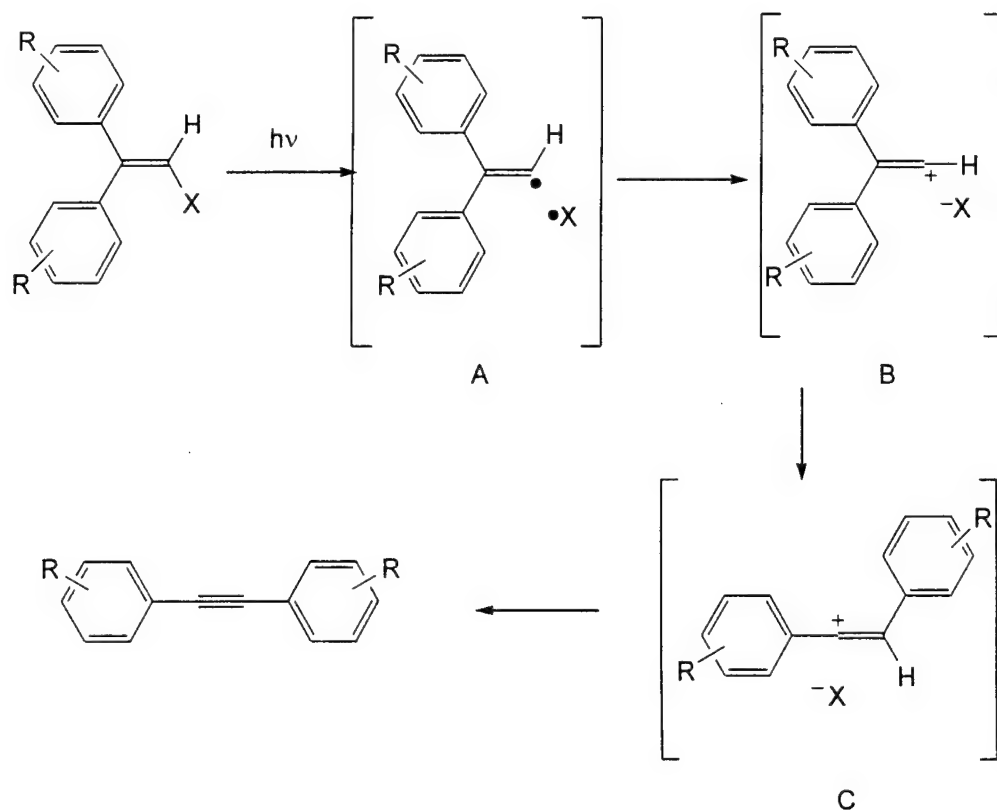
reported to have minimal weight loss even at 260 °C for 200 hours. A reduction in the IR band at 980  $\text{cm}^{-1}$  ( $\text{C}=\text{CCl}_2$ ) was reported along with the formation a new band at 1670  $\text{cm}^{-1}$ . This new band was attributed to the oxidation of the carbon-carbon double bond to a ketone. While a small amount of crosslinking may take place prior to decomposition it does not seem that this reaction would be the source of the exothermic decomposition. For the bisphenol C polycarbonate decomposed under nitrogen the band at 974  $\text{cm}^{-1}$  ( $\text{C}=\text{CCl}_2$ ) did not show a significant reduction even at temperatures up to 463 °C (peak of exotherm) although a new band at 1654  $\text{cm}^{-1}$  appeared. This new band could be attributed to changes in substituents on the aromatic ring, such as from a rearrangement that is similar to that obtained from a photo-Fries type rearrangement,<sup>35</sup> which shows a similar change in the IR spectra for polyarylates.<sup>36</sup>

1,1-Dichloro-2,2-diarylethylenes have been shown to undergo reactions to give acetylenes by a Fritsch-Buttenburg-Wiechall rearrangement.<sup>37</sup> The mechanism is proposed to be the elimination of both chlorines by a strong base to yield the carbene followed by a 1,2-aryl migration although no evidence for the carbene formation was reported (Figure 3.21). The highly reactive carbene probably rapidly undergoes the rearrangement to the acetylene after the loss of chlorine. For the polymers, this reaction may take place by the loss chlorine atoms which then scavenge hydrogen from the polymer to give HCl. The acetylene formed can undergo an exothermic crosslinking reaction since the loss of chlorine occurs at high temperature.

Vinyl bromides and chlorides have also been shown to undergo a photochemical reaction to yield an acetylene.<sup>38,39</sup> A proposed mechanism is shown in Figure 3.22. A similar type of mechanism can be envisioned for a 1,1-dihalo-2,2-diarylethylene. The



**Figure 3.21** Proposed mechanism for the formation of acetylene from 1,1-dichloro-2,2-diarylethylene.<sup>37</sup>



**Figure 3.22** Proposed mechanism for the formation of acetylene from a vinyl halide.<sup>39</sup>

halide bond is cleaved to yield the radical intermediate, A, which then undergoes an electron transfer to give, B, followed a 1,2-phenyl migration. Intermediate C can undergo dehydohalogenation to yield the acetylene. Only the final products from the photochemical reactions were identified; no evidence for any of the intermediates was reported.

Neither reaction described above has been shown to be thermally activated although both mechanisms seem feasible. For polymers prepared via interfacial polymerization techniques there is always a possibility of ionic impurities which might be able to activate this process. Thermally-initiated ionic intermediates have been proposed for decomposition pathway of poly(vinyl chloride).<sup>40</sup>

The formation of HCl was considered as a possible explanation for the exothermic heat evolved. The heat of formation of HCl from hydrogen and chlorine is -22 kcal/mol (-92 kJ/mol). Since two moles of HCl are formed for each repeat unit (307 g/mol) of polycarbonate, the heat of formation of HCl is approximately 600 J/g based on the total polymer mass. Using the value of the heat of decomposition for bisphenol C polycarbonate of 350 J/g and assuming that the baseline is from an endothermic type decomposition (use 200 J/g from bisphenol A polycarbonate), the net heat of decomposition becomes 550 J/g. This value is very close to the value for the heat of formation of HCl from the polymer (600 J/g). Also, if the formation of HCl is the source of the exothermic reaction it would correspond to the simultaneous weight loss observed.

From IR and Raman studies of the degraded polymers it was not possible to identify a mechanism. If crosslinking were the mechanism it would not necessarily lead to simultaneous weight loss. Also, a crosslinking reaction might be difficult due to steric

hindrance of the tetrasubstituted double bond. The degradation to yield an acetylene that undergoes an exothermic crosslinking reaction is possible although no spectroscopic evidence was obtained to confirm this as a possible mechanism. This could be due to the high reactivity of the intermediates. Bisphenol C monomer undergoes an exothermic reaction but at a substantially lower temperature than the polymers. This is thought to be in part due to the phenolic hydrogens playing a role in the decomposition.

Due to the fact that during thermal decomposition there is almost no monomer produced and a reduced amount of phenol is generated when compared with other bisphenol A polymers, it might be assumed that the dichloroethylidene group (or the product from its degradation) causes an efficient charring reaction to occur. The study of blends of bisphenol C polyarylate, poly-**2**, with other bisphenol A based polymers shows that more bisphenol C monomer is generated during the degradation of these blends. The appearance of more bisphenol C at lower concentrations in the materials implicates the dichloroethylidene group in the charring reaction. The fact that there is more char generated for polyarylate blends than for the copolymers implies that there may be some effect due to the proximity of the reactive dichloroethylidene groups. The respective  $T_g$ 's for the two polyarylate homopolymers are too close to determine whether there was any phase separation in the blends. The blends of poly-**2** with bisphenol A polysulfone showed two glass transition temperatures in DSC thermograms indicating that these blends are phase separated. Poly-**2** with bisphenol A polysulfone showed the greatest char yield enhancement whereas the addition of BPC (**II**) or DPE-BPC (**V**) did not have any effect on the char yield. These small molecules appear to well dispersed in the polymer since no melt transition was observed for either of the blends.



The generation of toxic products from the decomposition of halogenated materials is a major concern. It has been thought that the decomposition of dichloroethylidene ( $C=CCl_2$ ) containing materials could generate phosgene from the oxidation of the double bond. Experiments were performed to test for the presence of phosgene by researchers at General Electric.<sup>41</sup> Of the three samples tested, only one had positive results for trace amounts of phosgene (0.1 ppm). Pyrolysis-GC/MS showed no presence of phosgene in the decomposition products. The lack of phosgene could be because none is generated or that it is reactive or unstable and does not make it to the MS detector. A significant amount of HCl was detected by pyrolysis-IR whereas no HCl was detected during pyrolysis-GC/MS tests which is probably due to an interaction with the GC column. The toxicity of burn gases from bisphenol C polycarbonate (BPC-PC) materials on laboratory rats was reported in the literature.<sup>24</sup> The products from the air pyrolysis of 85/15-BPC/BPA copolycarbonate were found to be less toxic than those from bisphenol A polycarbonate (BPA-PC) and fire-retarded ABS (20 % Cl as PVC).

### **3.6 Conclusions and Recommendations**

Bisphenol-C-based polymers have exceptional fire-resistant properties, at least when measured by PCFC. The main drawback of these materials is that they are halogenated. While the high chlorine content imparts some of the fire resistance, other factors such as high char yield and the relatively slow decomposition rate play an important role. Determination of an exact mechanism for the charring reaction could aid in the design of new, non-halogenated polymers with similar fire-resistant properties.

### 3.7 Experimental Section

Simultaneous thermogravimetry-differential scanning calorimetry (TGA-DSC) thermograms were obtained using a Rheometrics STA 1500. Data were obtained at a heating rate of 10 °C/min under a 50 cc/min flow of dry nitrogen. The samples were run in an open alumina crucible. Heat flow was calibrated using a sapphire standard and the temperature was calibrated using a two point calibration with lead and zinc as the standards. A positive peak corresponds to an exothermic reaction or transition. Heat flow data is reported as normalized to initial sample mass, unless otherwise noted.

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) data was obtained using a CDS Analytical Pyroprobe 2000 with a CDS 1500 Valved Interface coupled to a Hewlett-Packard 5890 Series II Plus Gas Chromatograph/ 5972 Series Mass Selective Detector. The samples were heated in a quartz tube at 10 °C/ms to 1200 °C and then held for 30 seconds. The interface temperature and the GC inlet temperature were 280 °C. The initial temperature of the GC oven was 40 °C. The temperature was ramped at 10 °C/min to 290 °C and then held. The helium flow rate was 1 mL/min. The GC column was a capillary column, HP5-MS (crosslinked 5% PH Me Siloxane; 30 m x .25 mm).

Infrared data on solid char samples was obtained at Markem Corporation, Keene, NH, using a Matson Polaris FTIR coupled to a ATI Matson Quantum IR Microscope. Data was obtained in transmission mode on neat samples that were pressed between two diamond disks. The gas-phase IR data was obtained by Michael Ramirez at the FAA using a Nicolet Magna 500 FTIR. Samples were pyrolyzed using a CDS pyroprobe. Raman spectra were obtained using a Bruker FRA 106 FT-Raman spectrometer. ESCA

experiments were done using a Physical Electronics 5100 XPS. The results are from a 75 ° take-off angle and the source was Mg X-rays.

Pyrolysis-combustion flow calorimetry experiments were done at both the FAA and at the University of Massachusetts-Amherst. A description of the apparatus and the principles of use will be published in the near future.<sup>31</sup> Data was obtained at a heating rate of 4.3 K/s to a final temperature of 930 °C.

### **3.7.1 Materials**

The synthetic procedures for preparing polymers discussed in this section are given in Chapter 2. Structures for the polymers are shown in Appendix A. Commercially available polymers were obtained from the Aldrich Chemical Company. These include bisphenol A polycarbonate and bisphenol A polysulfone resin.

#### **3.7.1.1 Preparation of Blends**

Blends were prepared by dissolving appropriate amounts of each of the materials in methylene chloride or tetrahydrofuran. Solutions were cast onto glass microscope slides and then dried under vacuum at 70 °C for a minimum of 24 hours.

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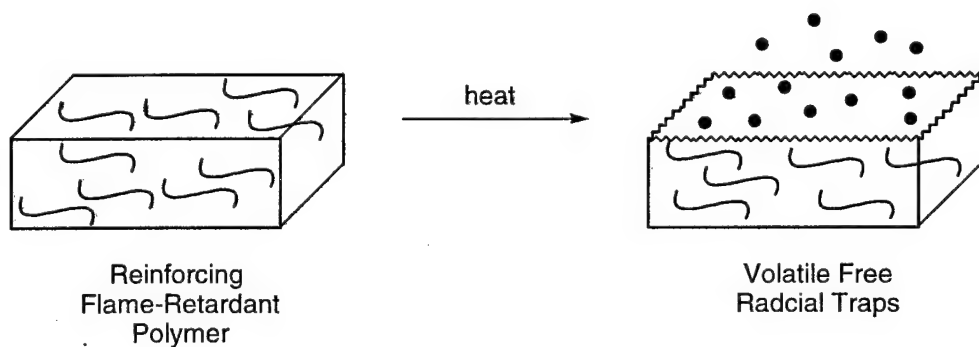
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## CHAPTER 4

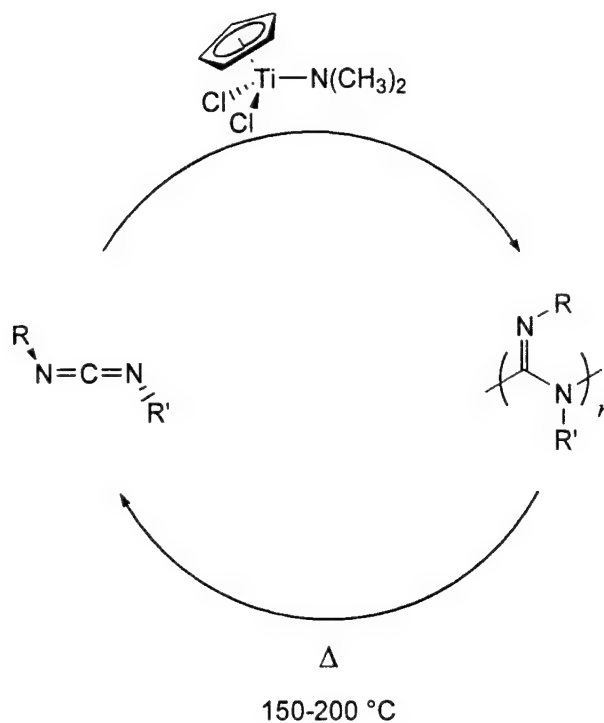
### POLYCARBODIIMIDES: AN APPROACH TO LATENT FIRE-RETARDANT POLYMERS

#### 4.1 Introduction

To address deficiencies in current additive-type flame retardants, we designed and studied polymers that have good mechanical properties throughout their lifetimes, but upon the application of thermal stress, decompose to monomeric flame retardants (Figure 4.1). We chose to study polycarbodiimides as prospective candidates because of their controlled decomposition back to monomer at temperatures in the range 150-200 °C (Figure 4.2). Additionally, the polycarbodiimide backbone contains no hydrogen and has a minimal carbon content ( $N/C$  ratio = 2) which efficiently reduces its potential



**Figure 4.1** Schematic of latent polymeric fire-retardant mechanism.



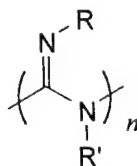
**Figure 4.2** Schematic of decomposition of polycarbodiimides.

fuel content. The substituents targeted included inorganic rings (phosphazenes, siloxanes), organohalogens and stable free radical moieties.

## 4.2 Results and Discussion

### 4.2.1 Synthesis of Materials

Polycarbodiimides with the structure



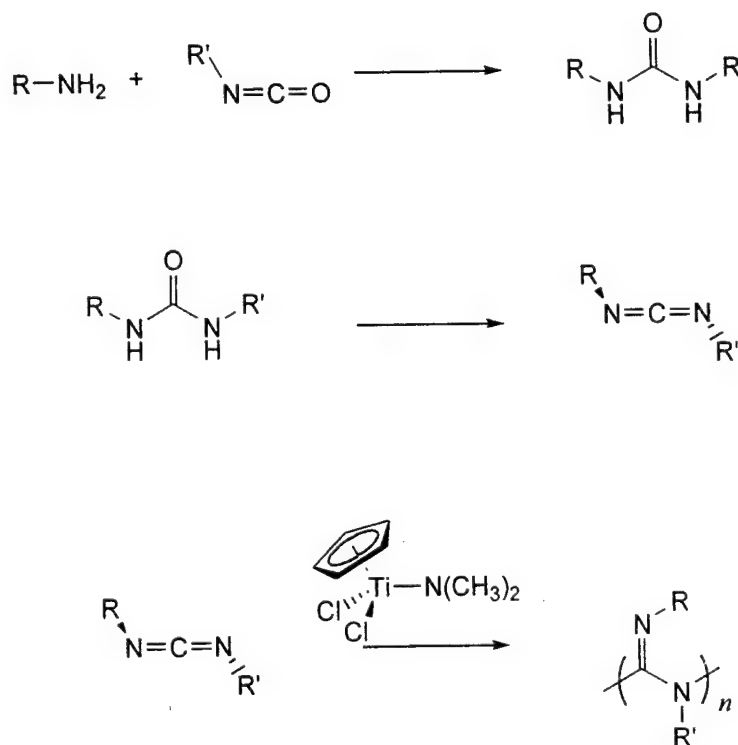
were first synthesized by Robinson via the anionic polymerization of carbodiimides.<sup>1</sup>

However, materials prepared by this method were generally only oligomers. Subsequent



work has focused on transition-metal-catalyzed polymerization of carbodiimides to yield high-molecular-weight polymers.<sup>2-4</sup> Goodwin *et al.* showed that a variety of carbodiimide monomers with various substituents could be polymerized using titanium catalysts.

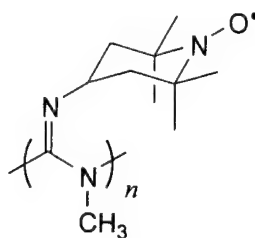
A general scheme for preparing polycarbodiimides is shown in Figure 4.3. The carbodiimide monomer is obtained in a two-step reaction. First an amine and an isocyanate are allowed to react to yield the corresponding urea. Using a procedure of Palamo, the carbodiimide is obtained by dehydrating the urea using bromotriphenylphosphonium bromide in methylene chloride.<sup>5</sup> The carbodiimide monomer can then be polymerized using a titanium catalyst, either as a neat liquid or in solution.



**Figure 4.3** General scheme for synthesizing polycarbodiimides.

Attempts were made to prepare carbodiimides with phosphazene, chlorinated aromatic, fluorinated aliphatic and triazine side-chain substituents. Failure to prepare targeted monomers was due to a variety of problems including insolubility of the urea, stability of substituted amine or isocyanate and decomposition of urea during the dehydration reaction.

A polycarbodiimide containing a stable free radical (poly-**19**) was synthesized. This polymer was prepared by methods described above for other polycarbodiimides. Electron spin resonance (ESR) spectroscopy was used to verify the presence of free radicals in the polymer (Figure 4.4). The ESR spectra for the TEMPO carbodiimide monomer is a triplet which is typical of the  $2(N)+1$  splitting pattern observed for TEMPO moieties. As expected, poly-**19** showed the presence of free radicals although the line shape and splitting was different. This was attributed to interaction of free spins due to close proximity and/or retarded diffusional effects in the polymer system.



poly-**19**

The degradation behavior of poly-**19** along with several other polycarbodiimides (Table 4.1) was studied using STA. GC/MS was used to identify the products from decomposition. These results are described in the following section.

**Table 4.1** Other polycarbodiimides synthesized.

	R	R'
poly-20	methylbenzyl	methyl
poly-21 ( <i>copolymer</i> )	TEMPO & methylbenzyl	methyl
poly-22	pentafluorophenyl	<i>n</i> -hexyl
poly-23	<i>n</i> -hexyl	<i>n</i> -hexyl

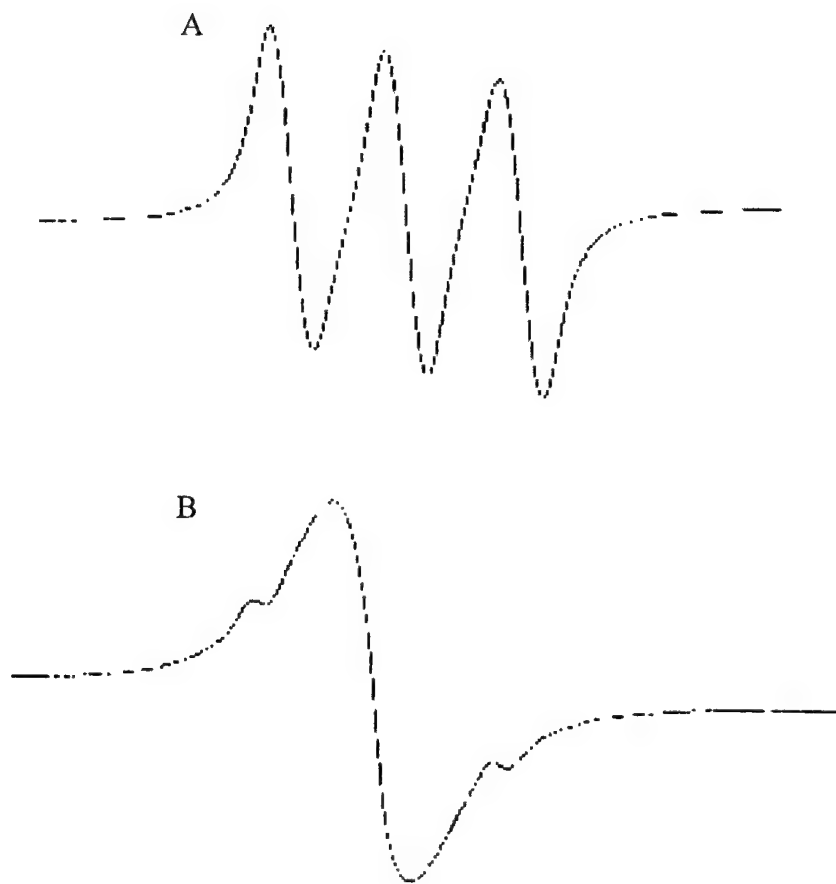
#### 4.2.2 Thermal and Mechanical Properties

For all of the polycarbodiimides studied, none of them showed any glass transition or melting prior to decomposition. It was possible to form transparent free standing films from poly-20 by spin coating glass plates with a polymer solution. Once all of the solvent was removed, the film was easily removed from the glass substrate. For poly-22, the film was a waxy substance once all of the solvent was removed. It was not possible to prepare films from this polymer.

Preliminary mechanical properties were obtained for poly-20 on the films prepared. The film tested was approximately 30 microns in thickness. Sample specimens were prepared of length 4 cm and width 1 cm. The samples were brittle with less than 2 % elongation at break. The tensile strength and the modulus were found to be  $39 \pm 3$  MPa and  $2.7 \pm 0.1$  GPa, respectively.

#### 4.2.3 Decomposition Behavior of Polycarbodiimides

The degradation behavior of polycarbodiimides was studied using STA. The two TEMPO-containing polymers degraded in an exothermic fashion whereas the other three polymers degraded endothermically. The initial degradative weight loss was very rapid



**Figure 4.4** ESR spectra for TEMPO containing materials. (A) Monomer **IX**. (B). Poly-19.

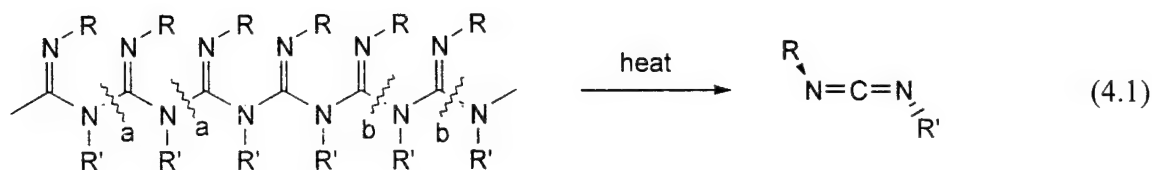
for poly-19. The peak mass loss rate for poly-19 was nearly three times faster than the other polymers that decomposed endothermically. The decomposition of poly-21, the copolymer, had a two stage decomposition with the first stage being exothermic and the second stage being mildly endothermic. The highest onset of decomposition observed for the polycarbodiimides was 200 °C. All of the polymers that decomposed endothermically showed 100 % weight loss. The two TEMPO-containing polymers had small char yields of only a few weight percent.

**Table 4.2** Summary of STA results for polycarbodiimides.

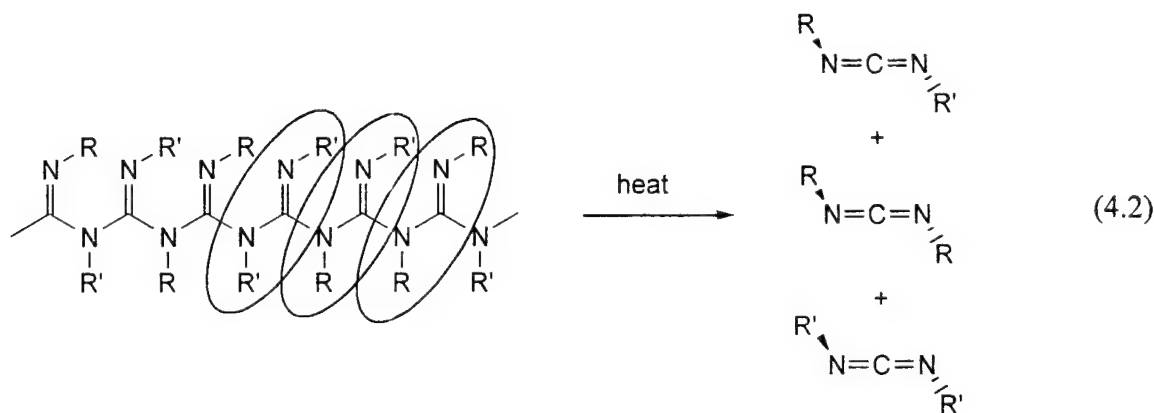
	Heat of Decomposition (J/g) <sup>a</sup>	Temperature at Peak in DSC Trace (°C)	Onset of Decompositio n (°C)	Temperature at Maximum in Weight Loss (°C)	Maximum Rate of Mass Loss (%/s)
Poly-19	+ 930	196	193	195	0.95
Poly-20	- 470	218	183	217	0.35
Poly-21	+ 554	---	183	---	---
Poly-22	- 450	221	176	224	0.31
Poly-23	- 353	231	200	239	0.39

<sup>a</sup> A (+) sign indicates an exothermic transition and a (-) indicates an endothermic transition.

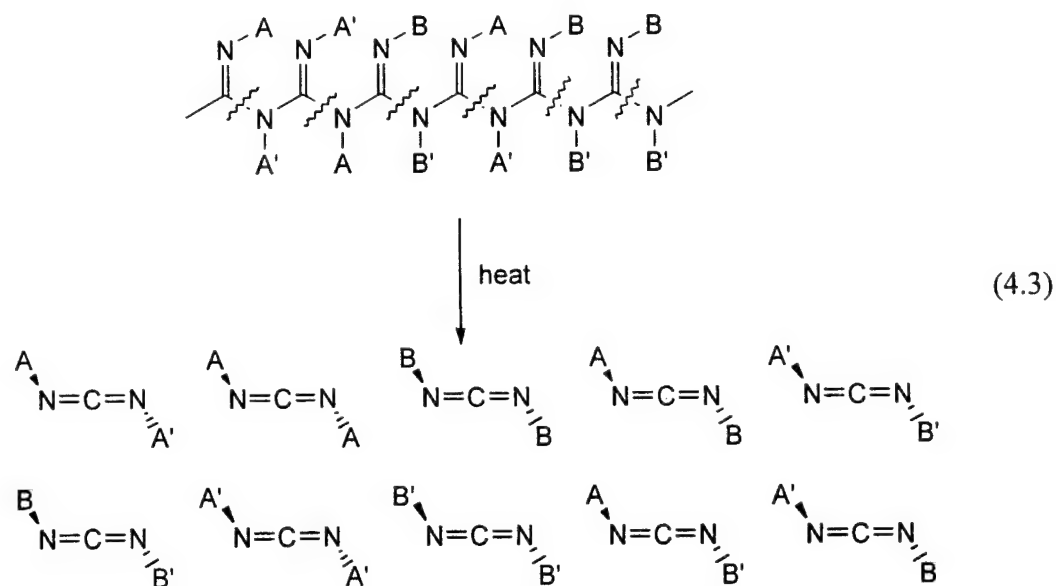
Robinson reported the polycarbodiimides degraded cleanly to yield carbodiimide small molecules.<sup>1</sup> This observation was also reported by Goodwin.<sup>3</sup> For a polymer where R = R' or where the monomer was inserted into the polymer with regiospecific preference, only the original monomer is generated during the decomposition as shown in the following equation



An  $^1\text{H}$  NMR spectra of the resulting degradation products was identical to that of the starting monomer, for the poly(di-*n*-hexyl)carbodiimide. For the decomposition of poly-**20**, only the original polymer was observed indicating a regiospecific polymer. In some cases, where the substituents were not the same, the degradation products were a mixture of metathesis products (i.e., carbodiimides resulting from the exchange of the carbodiimide substituents) as seen in Eq. 4.2. For random copolymers, where the



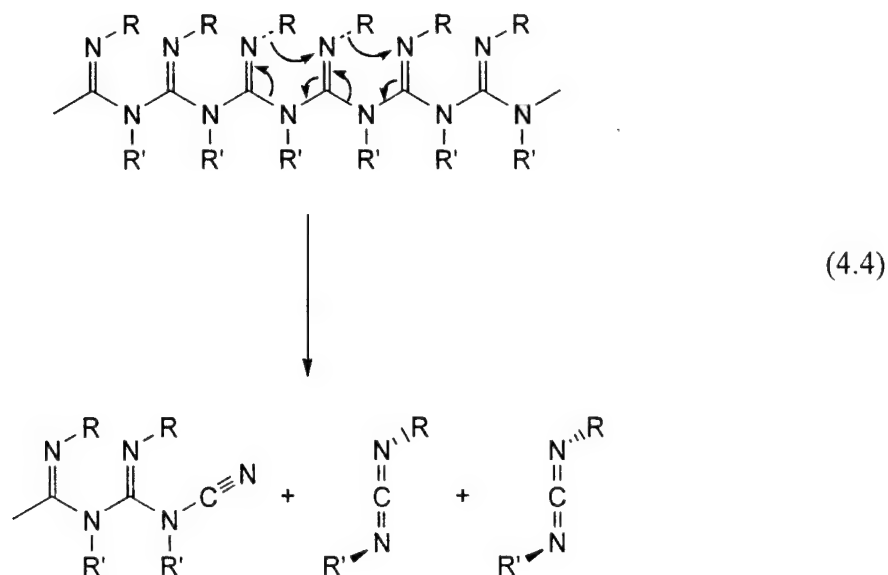
monomers are inserted in a nonregiospecific manner, many products could be envisioned from metathesis products of each of the monomers to cross-products containing substituents from both monomers (Eq. 4.3).



In the previous discussion, the decomposition of the polycarbodiimide is assumed to occur by a homolytic cleavage of the backbone bond followed by subsequent unzipping via a radical process. The decomposition of the polycarbodiimides at temperatures around 180 °C would be consistent with an activation energy of about 35 kcal/mol.<sup>6</sup> This activation energy is significantly lower than that calculated for the C-N backbone bond (67-86 kcal/mol, depending on substituents). A concerted mechanism for decomposition was proposed. The C-N backbone bond had a calculated activation energy of 33.2 kcal/mol for the concerted decomposition mechanism which is more consistent with the actual measured decomposition temperature.

Whether the decomposition occurs through an unzipping process or a concerted reaction, large amounts of monomer will be generated. Also, metathesis products can be formed by the concerted mechanism for copolymers and nonregiospecific polymers.

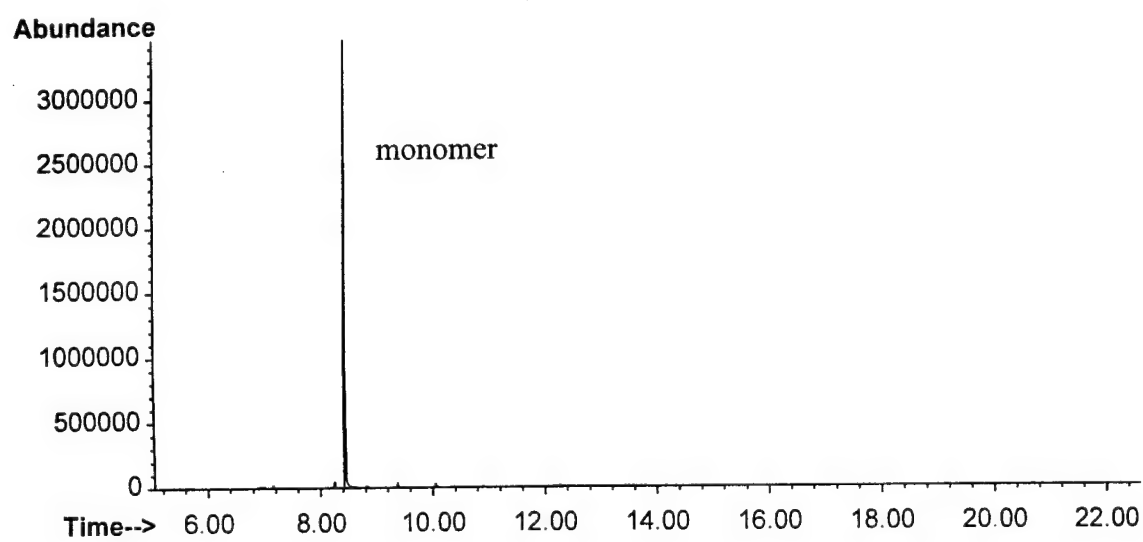
Here polycarbodiimides in solution were injected directly into a GC/MS. Since the injection port was hotter than the temperature of degradative weight loss, it was



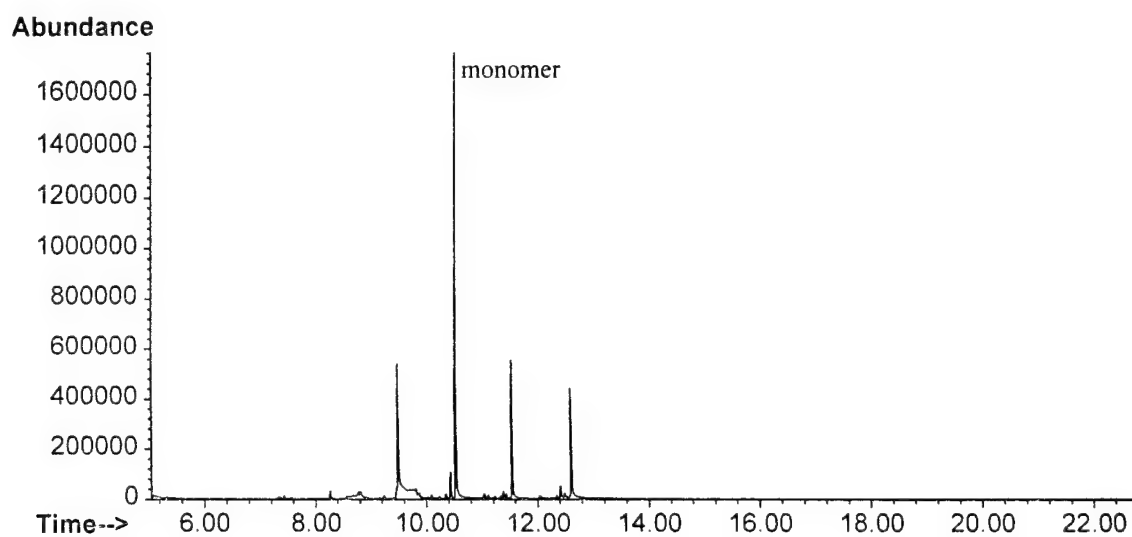
possible to analyze the products. For poly-**20**, the only product was N-methyl-N'-methylbenzyl-carbodiimide; the original monomer (Figure 4.5). The corresponding MS was identical to that of the starting monomer. This observation is also true for poly-**22** and poly-**23**.

Since the TEMPO containing polymers did not show 100 % weight loss, the polymers were heated at 300 °C in a sublimator under vacuum. The decomposition products were collected on the cold finger (-78 °C) and then dissolved in ether. The GC trace for the poly-**20** contains several components. The original monomer is one of the main components. For the copolymer, poly-**21**, both of the original monomers were identified as decomposition products. The other products generated during the decomposition were not able to be identified. These products did not correspond to metathesis products that can be formed from copolymer decomposition. This result is





**Figure 4.5** A GC trace of products from the decomposition of N-methyl-N'-methylbenzyl-polycarbodiimide (poly-20).

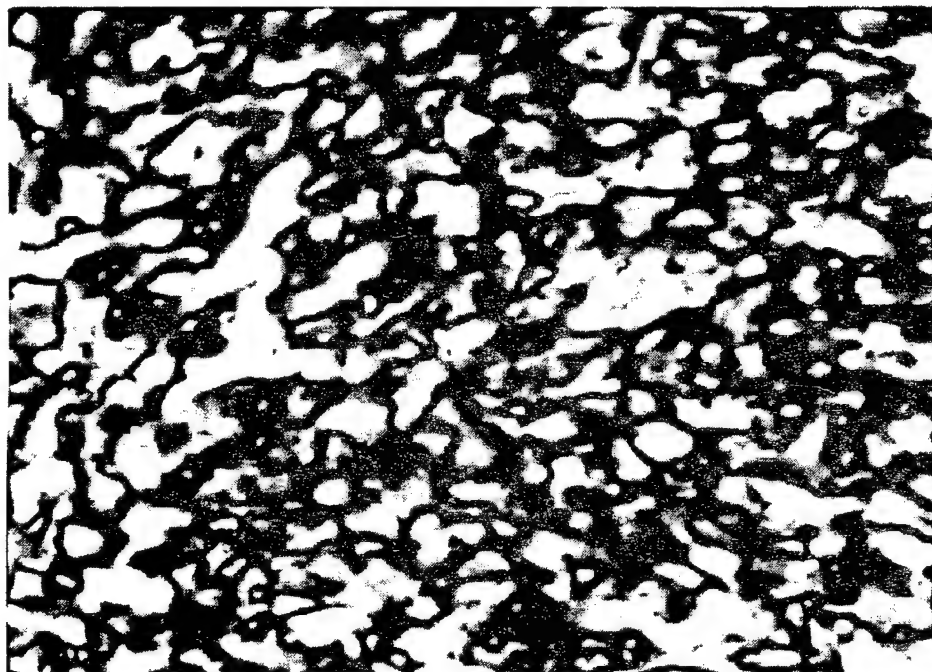


**Figure 4.6** GC trace of products from the decomposition of N-methyl-N'-TEMPO-polycarbodiimide (poly-19). The polymer was decomposed in a sublimator under high vacuum and the products were collected on the cold finger at -78 °C.

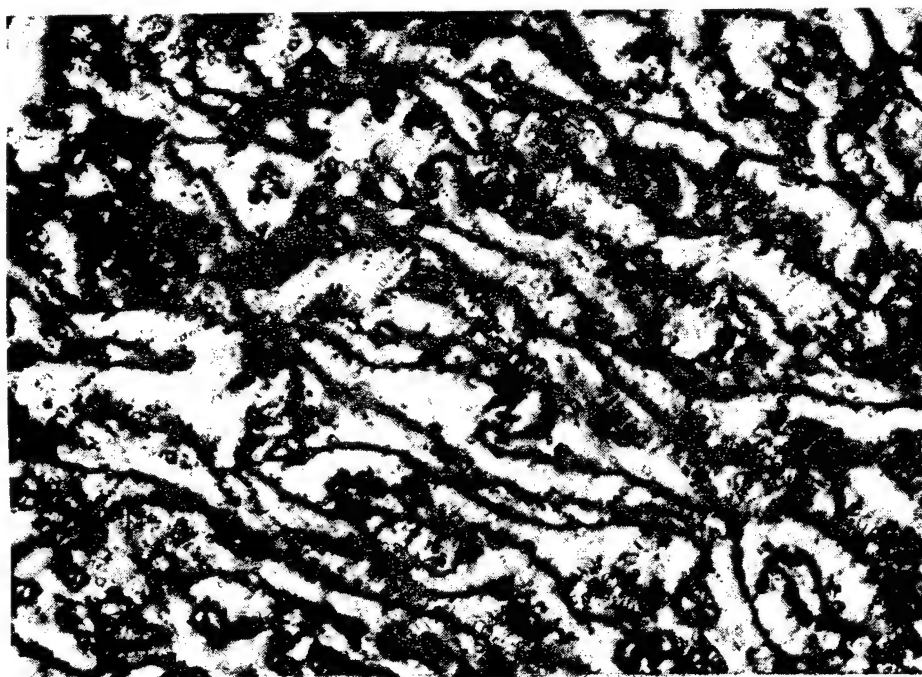
probably due to the fact that for both monomers one of the substituents is a methyl group that is much smaller than either the TEMPO or methylbenzyl substituent. Therefore, as was reported previously, both monomers may insert in a regiospecific fashion and therefore no metathesis or cross-products would be observed.

#### **4.2.4 Liquid Crystallinity of Polycarbodiimides**

Polycarbodiimides were found to have long persistence lengths, 400 Å.<sup>7</sup> These rigid-rod molecules were also found to exhibit lyotropic liquid crystalline (LC) behavior in a variety of solvents including toluene, chloroform and THF (Figure 4.7 and Figure 4.8). The polymer solutions formed nematic LC phases as evidenced by the formation of birefringence patterns. The viscous polymer solutions were pressed between two microscope cover slips. The samples then required a small amount of heating, 40-60 °C, in order to observe birefringence. The concentration at which liquid crystalline behavior was observed depended on the molecular weight of the sample. The exact molecular weight of polycarbodiimides is uncertain because of interactions with the GPC column but approximate molecular weights were determined using GPC-light scattering. The image shown in Figure 4.7 for poly-**20** at concentration of 20 wt% in chloroform. The molecular weight of this sample is on the order of 250,000 g/mol. For the same polymer with at molecular weight of 750,000 g/mol no birefringence was observed. Concentrations above 8 wt% of the higher molecular weight polycarbodiimide were gelled thus preventing further studies.



**Figure 4.7** Polarized optical micrograph of poly-20 in chloroform (20 wt%) at 40 °C (magnification = 380x).



**Figure 4.8** Polarized optical micrograph of poly-23 in chloroform (20 wt%) at 40 °C (magnification = 380x).

#### 4.2.5 Microcalorimetry Results

Peak heat release capacity for poly-**19** and poly-**20** were measured using PCFC (described in Chapter 3). The exact numbers cannot be directly compared with values reported in Chapter 3. The reason is that these polymers were tested when the technique was first being developed and lower pyrolysis temperatures and a different heating history were used when compared with current methods. Values obtained from PCFC for polycarbodiimides, poly-**19** and poly-**20**, along with a few other polymers are shown in Table 4.3.

**Table 4.3** PCFC results for polycarbodiimides and other commercial polymers.

Polymer	Peak Heat Release Capacity (J/g-K)
Polyethylene	622
Polymethylmethacrylate	281
Poly- <b>20</b>	246
Poly(ethylene terephthalate)	223
Poly- <b>19</b>	181
Polyphenylenesulfide	177
Polyetheretherketone	72
Polyimide	17

Due to the exothermic decomposition and the much more rapid weight loss, it might be expected the poly-**19** would perform worse than poly-**20**. For these polymers, this expectation was not found to be the case. When comparing poly-**19** with poly-**20**, the TEMPO-containing polymer the measured peak heat release capacity was decreased by 25 %. The reason for this modest reduction could be due to the small amount of char that is formed.

### 4.3 Conclusions

While neither of the polymers tested have sufficient properties to be considered flame retardant, it was interesting to find that the TEMPO-containing polycarbodiimide had a reduced peak heat release capacity. This reduction was unexpected considering that this polymer decomposed much more rapidly and in an exothermic manner.

The decomposition temperature appears to have some relation to the nature of the substituents. It is not evident whether the difference in decomposition temperatures is due to steric or electronic contributions. The fluorinated polycarbodiimide had the highest decomposition temperature even though it had two bulky substituents on both nitrogens.

### 4.4 Experimental

#### 4.4.1 General Section

All materials were obtained from commercial suppliers and used as received unless otherwise noted. Titanium catalyst, bischloro- $\eta^5$ -cyclopentadienyl-dimethylamido titanium(IV), ( $\text{TiCpCl}_2\text{N}(\text{CH}_3)_2$ ) was prepared according to literature procedures.<sup>8</sup> N-hexyl-N'-pentafluoro-polycarbodiimide (poly-24) was supplied by Dave Schlitzer at the University of Massachusetts-Amherst. Triphenylphosphine was recrystallized from hexane and stored under argon prior to use. Methylene chloride was dried with 4 Å molecular sieves. Toluene for polymerizations was dry and oxygen-free using a process described by Pangborn *et al.*<sup>9</sup> Chloroform for polymerizations was vacuum transferred from calcium hydride. Polymerizations were carried out in a MBraun Labmaster dry box under nitrogen atmosphere. Infrared spectra were recorded on a Perkin Elmer 1600

Series Fourier transform infrared spectrometer. GC/MS spectra were obtained using a Hewlett Packard 5890 Series II Plus gas chromatograph adapted with a Hewlett Packard 5972 Series Mass Selective Detector. Elemental analyses were performed on a Control Equipment Model 2XA elemental analyzer at the Microanalytical Laboratory Research Services, University of Massachusetts, Amherst, MA.

#### 4.4.2 Monomer Synthesis

**N-methyl-N'-( $\alpha$ -phenylethyl)urea (XI).**  $\alpha$ -Phenylethylamine (21.9 mL, 0.17 mol) and chloroform (200 mL) were added to a round bottom flask that contained a magnetic stir bar. The flask was cooled with an ice bath and then a solution of methylisocyanate (10 mL, 0.17 mol) in chloroform (15 mL) was added dropwise to the stirring amine solution. The mixture was stirred for 1 hour and the ice bath was then removed and stirring was continued for 1 hour. The chloroform was removed under reduced pressure and the resulting oily liquid solidified upon standing (yield = 29.9 g, 99 %).  $^1\text{H}$  NMR ( $d_6$ -acetone): 7.32 (m, 5H), 5.90 (br s, 1H), 5.37 (br s, 1H), 4.87 (m, 1H), 2.63 (d, 3H), 1.37 (d, 3H).

**N-Methyl-N'-( $\alpha$ -phenylethyl)carbodiimide (XII).** Carbodiimide **XII** was synthesized following a slight modification of literature procedures.<sup>4,5</sup> Triphenylphosphine (47.7 g, 182 mmol) was dissolved in 250 mL of methylene chloride and the reaction flask was cooled with an ice bath. Bromine (9.4 mL, 183 mmol) was diluted to 25 mL with methylene chloride and the resulting solution was added dropwise to the flask during which time a white precipitate formed in the solution. The solution was allowed to stir for 30 minutes and then triethylamine (55.7 mL, 400 mmol) was added to the flask.



Urea **XI** (20.2 g, 182 mmol) was added in several steps over a period of 45 minutes. One hour after the final addition of the urea, the reaction mixture was washed with water (3 x 250 mL). The organic layer was dried with magnesium sulfate and the methylene chloride was removed under reduced pressure. The residue was extracted with hexane. Removal of the hexane under reduced pressure yielded an oily liquid. Carbodiimide **XII** was purified by distillation under reduced pressure (40-42 °C/0.1 torr) and isolated as a clear, colorless liquid. Yield: 10.9 g (60 %) <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.34 (m, 5H), 4.63 (q, 1H), 2.90 (s, 3H), 1.47 (d, 3H).

**N-Methyl-N'-TEMPO-Urea (XIII).** 4-Amino-TEMPO (0.815 g, 4.8 mmol) was dissolved in chloroform (1 mL) and the resulting solution was cooled using an ice bath. Methyl isocyanate (0.280 mL, 4.8 mmol) was added dropwise to the rapidly stirring amine solution and the reaction was allowed to stir at room temperature for 8 hours. The chloroform was removed under reduced pressure to yield after recrystallization from DME the expected urea. IR (neat): 3405 (s), 3315 (s), 2978 (m), 2932 (m), 1635 (s), 1570 (s), 1458 (m), 1442 (m), 1365 (m), 1307 (s), 1241 (s), 1178 (m), 1086 (w), 1070 (w), 976 (w), 897 (w), 772 (w), 624 (m), 560 (w), 521 (w) cm<sup>-1</sup>. Anal. Calcd for C<sub>11</sub>H<sub>22</sub>N<sub>3</sub>O<sub>2</sub>: C, 57.87; H, 9.71; N, 18.40. Found: C, 57.67; H, 9.70; N, 18.40.

**N-Methyl-N'-TEMPO-Carbodiimide (XIV).** Carbodiimide **XIV** was synthesized using a procedure similar to that described for carbodiimide **XII**. The quantities of reagents employed were 1.9 g (72 mmol) of triphenylphosphine, 0.37 mL (72 mmol) of bromine, 2.2 mL (159 mmol) of triethylamine, 10 mL methylene chloride, 1.1 g (4.7 mmol) of crude urea **XIII** and 30 mL of hexanes. The resulting carbodiimide was purified by vacuum sublimation at 50 °C/0.01 torr to yield an orange solid (yield =

0.25 g, 25 %). IR (KBr pellet): 2975 (m), 2934 (m), 2135 (s), 1686 (w), 1466 (m), 1365 (m), 1349 (m), 1244 (m), 1177 (m), 1010 (w), 986 (w), 963 (w), 696 (m), 620 (m), 566 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{11}\text{H}_{20}\text{N}_3\text{O}_1$ : C, 62.83; H, 9.59; N, 19.98. Found: C, 63.16; H, 9.38; N, 19.50. MS ( $m/z^+$ ) = 210.

**N,N'-di-*n*-hexyl urea (XV).** Urea **XV** was prepared by the same procedure described for urea **XI**. The quantities of reagents used were 15.9 mL (0.120 mol) of hexylamine, 17.5 mL (0.120 mol) of hexylisocyanate and 200 mL of chloroform. Yield = 26.8 g (98 %).

**N,N'-di-*n*-hexyl carbodiimide (XVI).** Carbodiimide **XVI** was synthesized using a procedure similar to that described for carbodiimide **XII**. The quantities of reagents employed were 34 g (0.13 mol) of triphenylphosphine, 6.75 mL (0.13 mol) of bromine, 40.3 mL (0.29 mol) of triethylamine, 200 mL methylene chloride, 20 g (0.088 mol) of crude urea **XV** and 100 mL of hexanes. Carbodiimide product was distilled under vacuum at 65 °C/ 100 mtorr. Yield = 13 g (70 %).

#### 4.4.3 Polymer Synthesis

**Poly(N-methyl-N'-TEMPO)carbodiimide (poly-19).** In a dry box, carbodiimide **XIV** (0.079 g, 0.37 mmol) and chloroform (150  $\mu\text{L}$ ) were added to a vial containing a stir bar. A catalyst solution of  $\text{TiCpCl}_2\text{N}(\text{CH}_3)_2$  (2.6 mg, 0.011 mmol) in toluene (0.500 mL) was prepared. Using a syringe, 55  $\mu\text{L}$  of the catalyst solution was transferred to the vial. The polymerization solution was allowed to stir in the dry box until solidified (overnight). The vial was then removed from the dry box and the polymer

was dissolved in chloroform, precipitated in methanol, filtered and dried (yield = 69.5 mg, 87 %).

**Poly(N-methyl-N'-phenylethyl)carbodiimide (poly-21).** In a dry box, carbodiimide **XII** (0.75 g, 0.0042 mol) and  $\text{TiCpCl}_2\text{N}(\text{CH}_3)_2$  (3.3 mg, 1.4 mmol) were added to a vial containing a stir bar. After stirring for about 5 min, the polymerization solution became too viscous to stir. The polymer was dissolved in toluene and then precipitated in methanol, filtered and dried. The isolated polymer was lyophilized from benzene.

**Copolymer from N-methyl-N'-phenylethyl-carbodiimide (VII) and N-methyl-N'-TEMPO-carbodiimide (IX) (poly-22).** Poly-22 was prepared by a similar procedure to that described for poly-20. The amounts of reagents used were 34.6 mg (0.165 mmol) of **XIV**, 26.3 mg (0.164 mmol) of **XII**, 200  $\mu\text{L}$  of toluene, and 22  $\mu\text{L}$  of catalyst solution (17.3 mg in 1 mL toluene). Yield = 46.3 mg (76 %).

**Poly(N,N'-di-*n*-hexyl)carbodiimide (poly-23).** Poly-23 was prepared by a similar procedure to that described for poly-21 except using carbodiimide **XVI** as the monomer.

## 4.5 References

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## CHAPTER 5

### SUMMARY AND RECOMMENDATIONS

#### 5.1 Overall Summary

In Chapter 1 the difficulty of obtaining fire-resistant polymeric materials was described. The problem lies in the fact that all organic polymers will burn when sufficient heat and oxygen is supplied. Therefore, the dilemma lies in developing and using materials to meet the potential risk. The problem is compounded for applications with limited egress, such as airplanes, submarines and subways. For aircraft applications, there is the additional issue of potentially large fires from the massive amounts of extremely flammable jet fuel.

For aircraft applications, the heat release rate of the interior materials is related to the escape time.<sup>1</sup> The more time for escape, the greater potential for lives saved. The Federal Aviation Administration has set a goal to develop materials with an order-of-magnitude reduction in the peak heat release rate of all materials used in aircraft interiors.<sup>1</sup> This goal includes a 50 % reduction in the heat release rate of cabin materials by the year 2005 and materials with zero heat release rate by 2018. The use of ultra-fire-resistant materials will provide a minimum of 10 minutes for passenger escape. In order to obtain this goal, the development of new materials as well as a detailed understanding of the physical properties and characteristics that contribute to a fire are required. The toxicity of the decomposition and combustion gases is also of great concern. Finally, the

processability and the cost of the new materials must be reasonable in order for their use to be considered.

In Chapter 2, the synthesis of the bisphenol-C-based polymers was discussed. As can be seen from the literature as well as the polymers described here, the bisphenol C monomer can easily be incorporated into thermoplastic materials. High-molecular-weight polymers were prepared using interfacial polymerization techniques. Transparent films of these polymers could be obtained from solution casting. The polyarylates based on bisphenol C had high glass transition temperatures ( $>200\text{ }^{\circ}\text{C}$ ). Some but not all of the bisphenol C polyarylates showed flow above their glass transition temperature. Aliphatic polyesters based on bisphenol C had much lower glass transition temperatures. These materials exhibited flow above their glass transition temperatures.

Important parameters contributing to the combustion of polymers include the nature of the decomposition products, the rate at which these products are released (mass loss rate) and how much mass is released (related to char yield). These parameters were investigated for bisphenol-C-based polymers and related materials and the results were reported in Chapter 3. From thermogravimetry analysis (TGA) results, it was found that the peak in the rate of mass loss was less and the char yields were greater for bisphenol C polyarylates when compared with corresponding bisphenol A polyarylates. Using simultaneous-TGA/DSC (STA), the heat of decomposition for bisphenol C materials was found to always occur in an exothermic manner. This result is in contrast to most polymers which decompose endothermically under inert conditions.

The char from bisphenol C polycarbonates at various stages during decomposition was analyzed using FT-IR, FT-Raman and Elemental Spectroscopy for Chemical

Analysis (ESCA). These methods yielded little information on the decomposition behavior of the polymers. Pyrolysis-GC/MS and pyrolysis-IR gave some of the most valuable information on the decomposition behavior of bisphenol C polymers. The presence of HCl in the decomposition products was shown using pyrolysis-IR while it was not detected in GC/MS, most likely due to an interaction with the column. The use of pyrolysis-GC/MS allowed for the identification and a qualitative comparison of the relative amounts of each of the products generated. As mentioned previously, the generation of highly toxic gases is a concern. Neither pyrolysis technique detected the presence of phosgene, which is a possible product from the decomposition of bisphenol-C-based materials.<sup>2</sup>

The effects of blending of bisphenol-C-based materials with other polymers was also studied. For the polymer blends, the addition of bisphenol C polyarylate had a enhancement in the char yield above that of what would be expected on a purely additive basis. The enhancement was not the same for all polymer blends with the greatest effect occurring in blends with bisphenol A polysulfone. The enhancement was found to occur at all compositions even down to 5 wt% loading. Small-molecule bisphenol C materials showed no enhancement in the char yield when blended with bisphenol A polysulfone.

The combustion properties for these materials were measured using a technique developed by researchers at the Federal Aviation Administration. Pyrolysis-Combustion Flow Calorimetry (PCFC) allowed for the determination of important combustion parameters, peak heat release capacity and total heat release, on small quantities of samples prepared in our laboratory. The peak heat release capacity for bisphenol C polyarylate was one of the lowest values measured at 18 J/g-K. Bisphenol-C-based

materials always had lower peak heat release capacities than related bisphenol A polymers. For the polyarylates, the peak heat release capacity was reduced from 420 J/g-K for the bisphenol A polymer to 18 J/g-K for the bisphenol C polymer. The much improved combustion properties of bisphenol C materials when compared with similar bisphenol A polymers can be attributed to several factors including increased char yields, decreased amounts of organic material generated (relative to amount of carbon dioxide generated), the larger amounts of non-combustible gases generated (HCl and carbon dioxide) and a reduction in the peak mass loss rate. The trend in the enhancement in the char yield was also found to occur in the peak heat release rate with the addition of bisphenol C moiety, as either polymer blends or co-monomer, having a much greater effect than a purely additive one. The nonlinear reduction in the peak heat release capacity can be attributed to the observed char enhancement and also the reduction in the peak mass loss rate.

The goal of the second project was to investigate the possible use of polycarbodiimides to generate flame retardants at elevated temperatures. As described in Chapter 4, this idea was not truly explored due to difficulties in synthesizing such polymers. The main observation that came about studying these materials was that the decomposition of a polymer could be exothermic and still have lower flammability measures, at least for the combustion test used. (This result was also observed latter for bisphenol-C-based polymers). Also, the substitution of a TEMPO stable free radical as a side chain on the polycarbodiimide showed a reduction in the peak heat release capacity.



## 5.2 Future Recommendations

While several bisphenol-C-based polymers were prepared and studied, a variety of other polymers could be prepared for comparison. The ester and carbonate groups seem to be weak links in the polymer backbone. This conclusion is based on the large amount of carbon dioxide generated during decomposition. Bisphenol-C-based polymers containing other functionalities, such as ether linkages, might lead to more thermally-stable materials with higher char yields and reduced flammability. Thermoplastic processing of bisphenol C polycarbonates has been demonstrated in the literature<sup>3</sup> but processing characteristics of bisphenol C polyarylates should be investigated.

Pyrolysis-GC/MS and PCFC were found to be valuable techniques in evaluating the small amounts of materials synthesized in the laboratory. Pyrolysis-GC/MS experiments were all performed at one heating rate and final temperature. This technique could be further developed to study the decomposition behavior of these materials as well as other polymers by pyrolyzing at various temperatures and heating rates and sampling at various stages during the decomposition. Also, the amounts of each product generated was based on the relative peak area. A more quantitative evaluation, either by approximation of fragmentation or by using a flame-ionization detector (FID), could give more detailed information on possible decomposition pathways.

Bisphenol-C-based polymers had some of the lowest peak heat release capacities measured by PCFC. The number of halogenated polymers for comparison is limited. In order to baseline these materials and determine a correlation with other medium-scale tests, additional halogenated polymers, with known flammability properties, need to be tested. Additionally, all of the materials tested and reported in the literature were of pure

polymers.<sup>4</sup> The effect of antimony oxide on the combustion properties of bisphenol C polyarylate was explored. The peak heat release capacity was greater for the polymer with antimony oxide which was attributed to an increase in the peak mass loss rate. Whether this result is real or an artifact of the test procedure is not known. PCFC experiments need to be performed on flame-retarded polymers for which flammability properties have been measured using other techniques. These experiments are needed to determine the validity of the PCFC test for the evaluation of additive-type flame-retardants in polymers.

A reduction in the combustion property, peak heat release capacity, can be attributed to several characteristics, such as char yield, peak mass loss rate and composition of decomposition products. Although the nature of decomposition (exothermic versus endothermic) was found not to have a large effect, the relative importance of the other characteristics still needs to be determined. While all of these parameters are important, it might be found that one characteristic has the greatest influence on reducing the flammability. Further studies on other materials could possibly lead to determining trends and levels of influence of the various polymer characteristics.

While blends with bisphenol C polyarylate were found to have enhanced char yields and reduced flammability properties, the mechanism for this observation has not been identified. The degree of enhancement in char appears to be related to the miscibility of the materials. Further investigation on the effect of miscibility of polymer blends on their interaction during decomposition would be interesting and could help in designing other flame-retardant polymer blend systems. Along these lines, the study of other blends, even those that do not include flame-retardant polymers, and their effects on

thermogravimetry and PCFC results could yield valuable information on what parameters contribute most to improved properties. For example, it might be found that the peak heat release rate could be decreased for blends where the two materials have peak mass loss rates at occurring different temperatures. This reduction would be akin to a simple dilution mechanism by a spreading out the temperature region where decomposition is occurring.

The presence of chlorine in these polymers is their biggest drawback, especially with many countries mandating a reduction in the use of halogenated materials because of concerns over post-consumer recyclability, generation of toxic products during incineration and landfilling. While materials used in aircraft are not considered disposable goods, there is still a concern over waste products during synthesis and toxic decomposition products. An investigation into other atoms/functional groups that could replace the chlorines but still have the same decomposition mechanism could be done. Synthesis of variations of the bisphenol could also give insights into the decomposition mechanism.

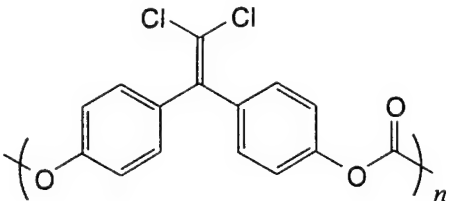
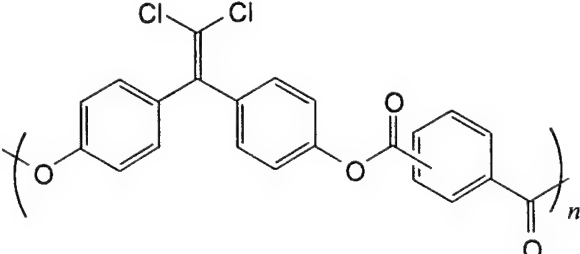
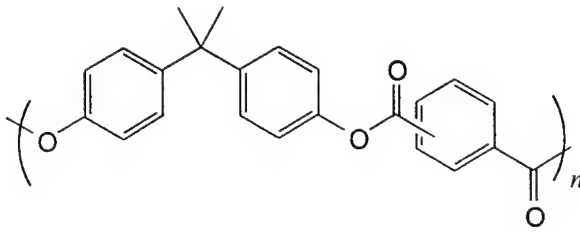
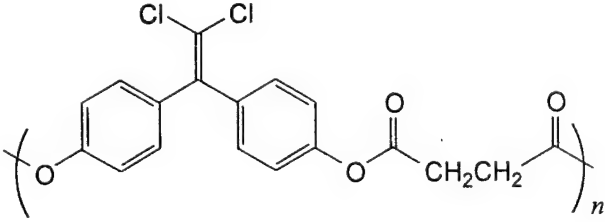
### 5.3 References

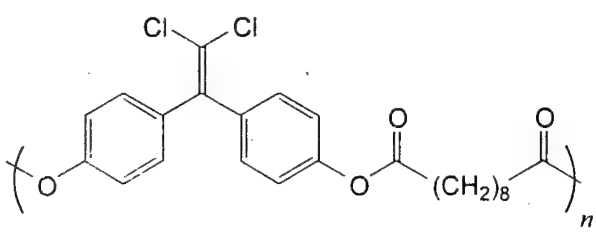
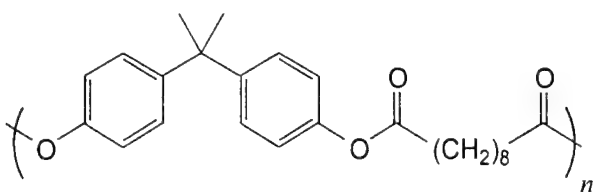
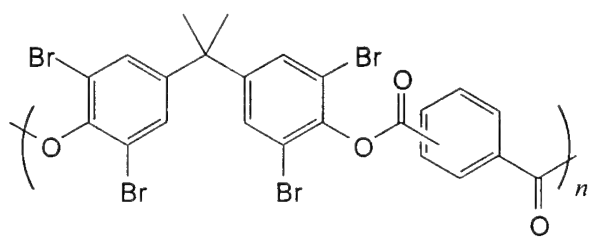
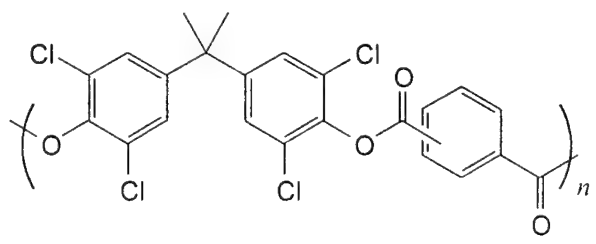
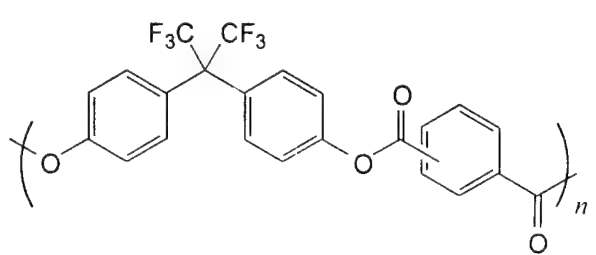
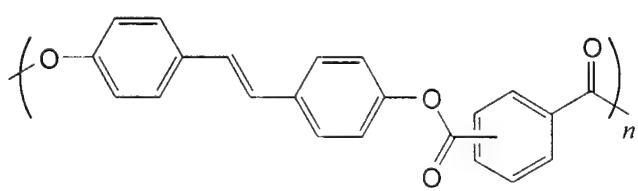
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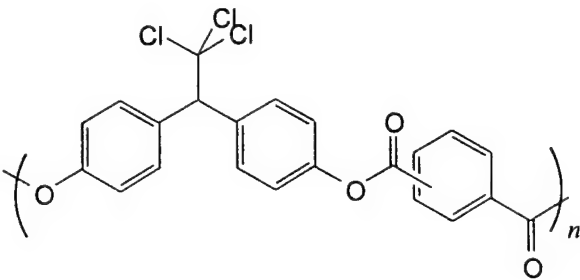
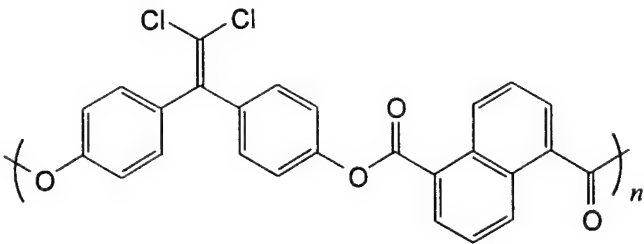
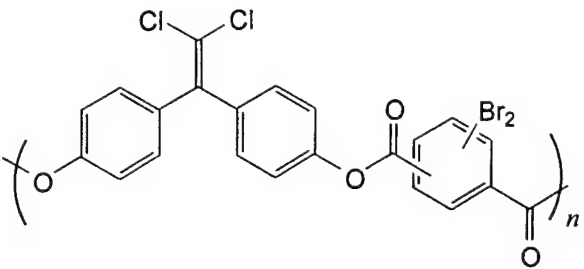
## APPENDIX A

### POLYMER STRUCTURES OF BISPHENOL-BASED POLYMERS

**Table A.1** List of polymer structures.

	Poly-1
	Poly-2
	Poly-3
	Poly-4

	Poly-5
	Poly-6
	Poly-7
	Poly-8
	Poly-9
	Poly-10

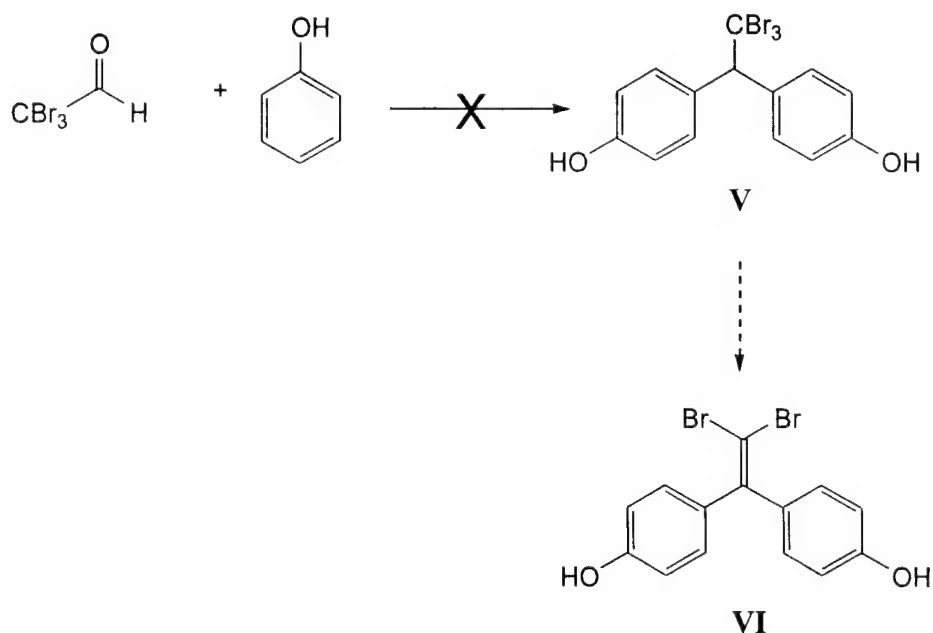
 <p>The structure shows a polymer repeat unit enclosed in large parentheses with a subscript <i>n</i>. It consists of a 4,4'-dichlorodiphenylmethane group (two benzene rings connected by a central carbon atom which has two chlorine atoms attached) linked via an ether bond to a 4,4'-oxydiphenyl dicarbonyl group (two benzene rings connected by an oxygen atom, with carbonyl groups at the 4 and 4' positions).</p>	Poly-11
 <p>The structure shows a polymer repeat unit enclosed in large parentheses with a subscript <i>n</i>. It features a 4,4'-dichlorodiphenylmethane group (two benzene rings connected by a central carbon atom which has two chlorine atoms attached) linked via an ether bond to a 4,4'-oxydiphenyl dicarbonyl group where the central ring is a naphthalene system.</p>	Poly-12
 <p>The structure shows a polymer repeat unit enclosed in large parentheses with a subscript <i>n</i>. It consists of a 4,4'-dichlorodiphenylmethane group (two benzene rings connected by a central carbon atom which has two chlorine atoms attached) linked via an ether bond to a 4,4'-oxydiphenyl dicarbonyl group where the central ring is a 2,5-dibromobenzene ring.</p>	Poly-13

## APPENDIX B

### ATTEMPTED SYNTHESIS OF BISPHENOL C RELATED COMPOUNDS

The reaction of bromal (1,1,1-tribromoacetaldehyde) with aromatic compounds has been reported in the literature.<sup>1,2</sup> Chlorobenzene, bromobenzene and anisole have all been reacted with bromal to form the related 1,1,1-tribromoethanes. The compound from the reaction of bromobenzene with bromal was reported to undergo decomposition by the elimination of hydrogen bromide.

An attempt was made to synthesis tribromide **V** by the same procedure described above for the bisphenol C using sulfuric acid in glacial acetic acid (Figure B.1). The product from this reaction did not precipitate from the acid solution as with the trichloride.

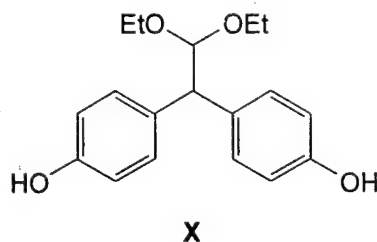


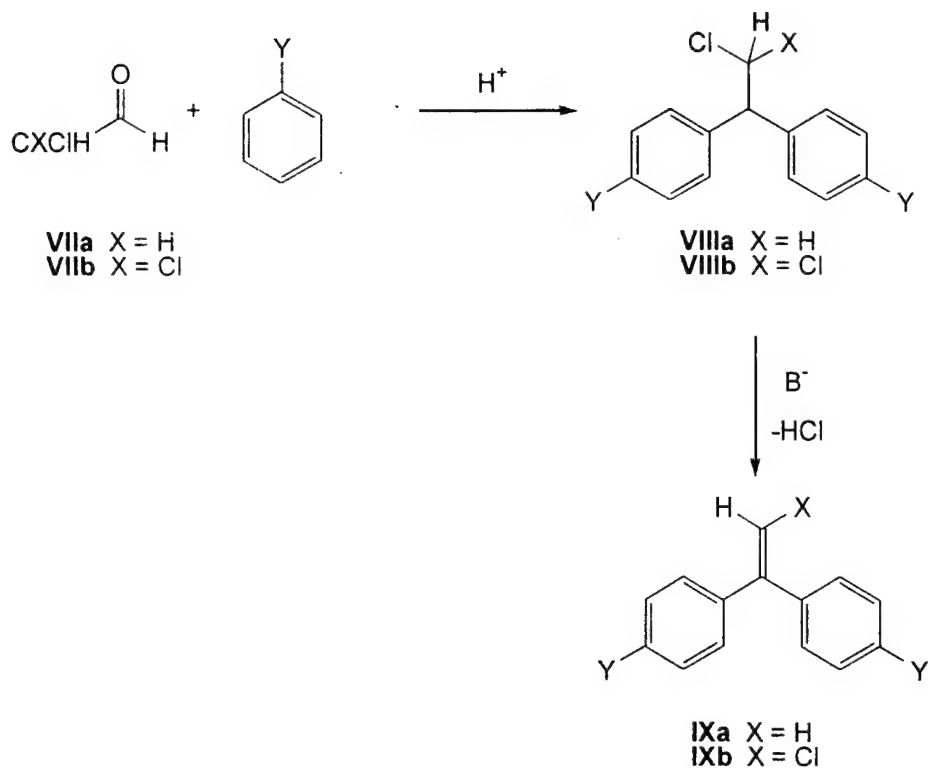
**Figure B.1** Schematic of proposed route to 1,1-dibromoethyldene-2,2-bisphenol (**VI**).



The reaction solution became a dark purple and very viscous. The resulting product, once precipitated in water, was a purple taffy-like substance and had a strong odor of bromal. Cristol *et al.* reported that the use of acetic acid results in the diacetate of bromal hydrate.<sup>2</sup> The use of methylene chloride as a solvent has been reported in literature for the condensation of trihaloacetaldehydes with aromatics.<sup>3</sup> The use of methylene chloride as the solvent also yielded a taffy-like product. One possible side reaction could be the substitution at another position on the aromatic ring. The use of an excess of phenol yielded a product that was solid but the product could not be isolated from the phenol.

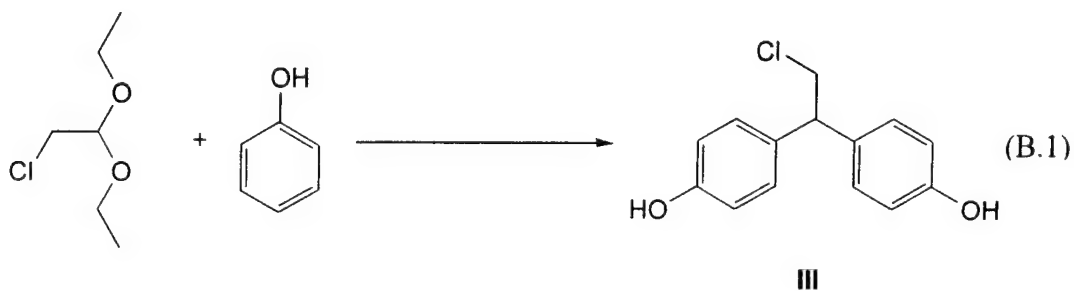
In addition to chloral, chloroacetaldehyde (**VIIa**) and dichloroacetaldehyde (**VIIIb**) have been reported to undergo condensation reactions with aromatic compounds in the same manner as chloral to form monochloride and dichloride products, respectively (Figure B.2).<sup>4-6</sup> The dehydrohalogenation of the dichloride **VIIIa** (where Y = OCH<sub>3</sub>, CH<sub>3</sub>, H, F, Cl, Br) to yield a vinylidene chloride **IXa** has been described in the literature.<sup>7</sup> For the case where Y = OH, researchers found that the attempted dehydrochlorination of the dichloride with potassium hydroxide in ethanol yielded a chlorine-free product.<sup>4</sup> The structure of the product was identified as the diethylacetal of bis(p-hydroxyphenyl)-acetaldehyde, **X**.





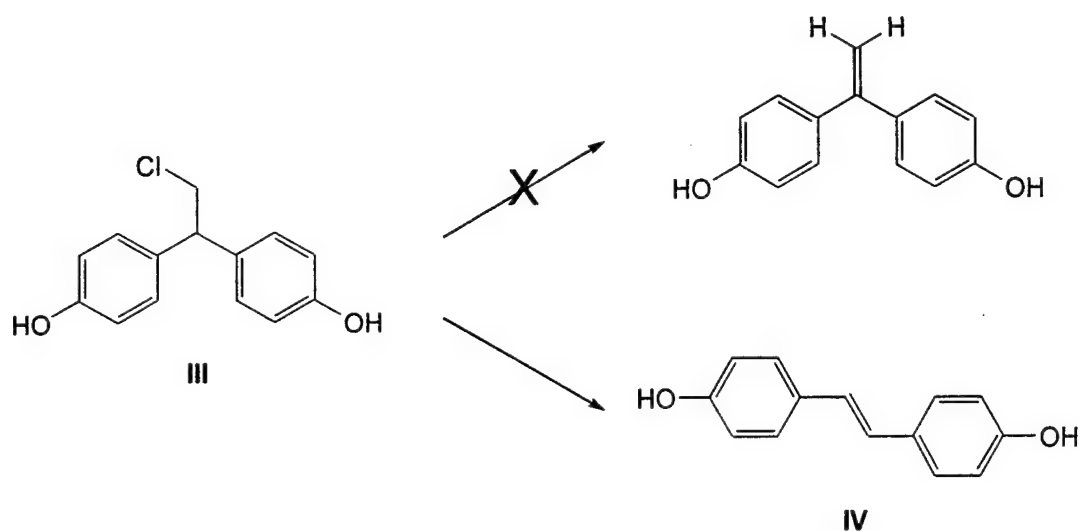
**Figure B.2** Reaction scheme for formation of ethylene and vinylidene chlorides by dehydrohalogenation of chlorinated ethanes.

The diethyl acetal of chloroacetaldehyde was allowed to react with phenol to give the desired product **III** in 50 % yield with the remaining product being a sticky pink solid (Eq. B.1). Attempts to dehydrochlorinate **III** generally led to multiple products that did



not include the desired product. For the dehydrohalogenation using LiCl in DMF, dihydroxystilbene was the main product obtained in about 50 % yield (Figure B.3).

When KOH in water was used to dehydrochlorinate **III** at 50 °C, a small amount of the stilbene **IV** was also isolated.



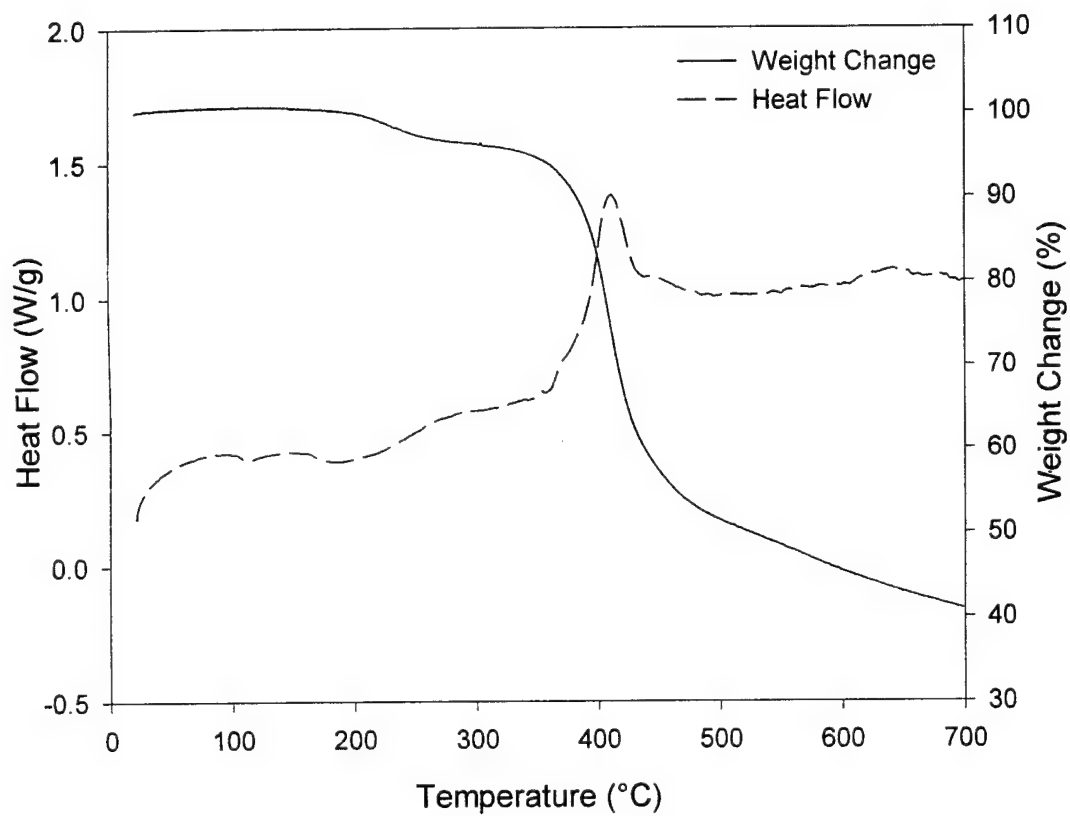
**Figure B.3** Dehydrohalogenation of monochloride.

## B.1 References

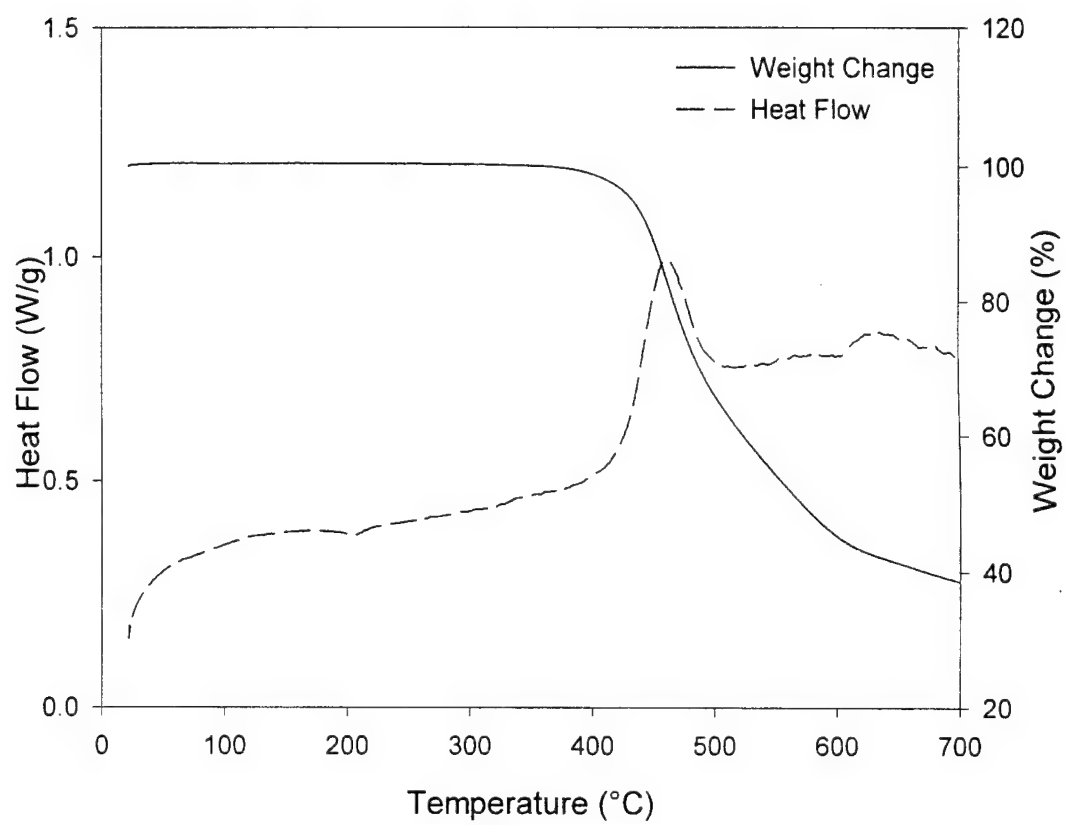
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2. Cristol, S. J.; Haller, H. L. *J. Am. Chem. Soc.* **1946**, 68, 140.
3. Campbell, J. R.; Klopfer, H. J. U.S. Patent 4,105,857, 1978.
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## APPENDIX C

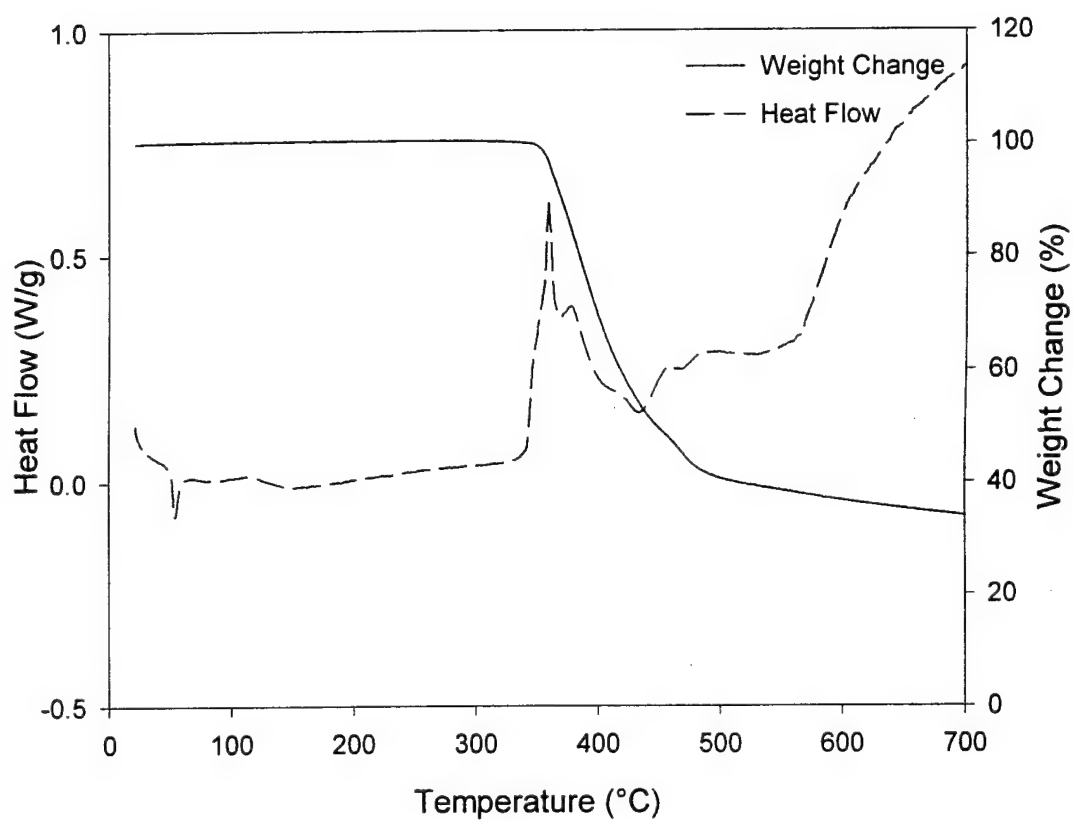
### SIMULTANEOUS-TGA/DSC THERMOGRAMS FOR BISPHENOL BASED MATERIALS



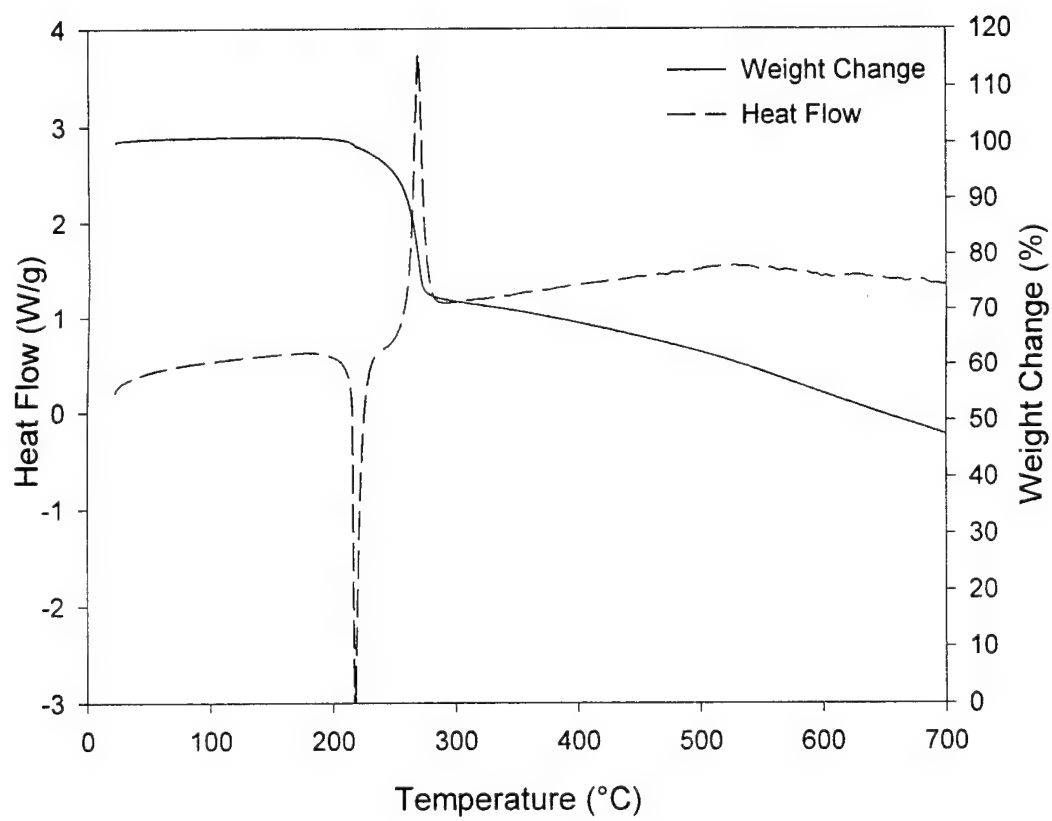
**Figure C.1** Simultaneous-TGA/DSC results for bisphenol C-succinyl polyester (poly-4).



**Figure C.2** Simultaneous-TGA/DSC results for bisphenol C-brominated polyarylate (poly-13).

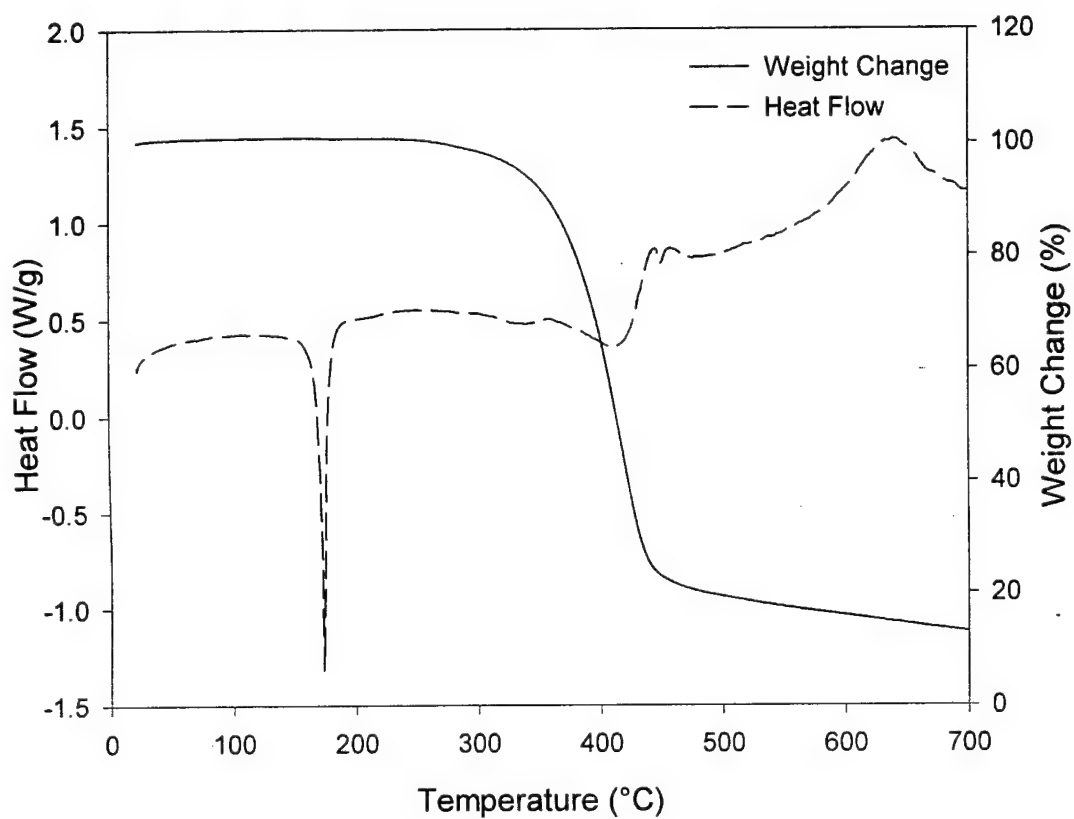


**Figure C.3** Simultaneous-TGA/DSC results for bisphenol C-sebacoyl polyester (poly-5). (Aged sample).



**Figure C.4** Simultaneous-TGA/DSC results for bisphenol C (II).

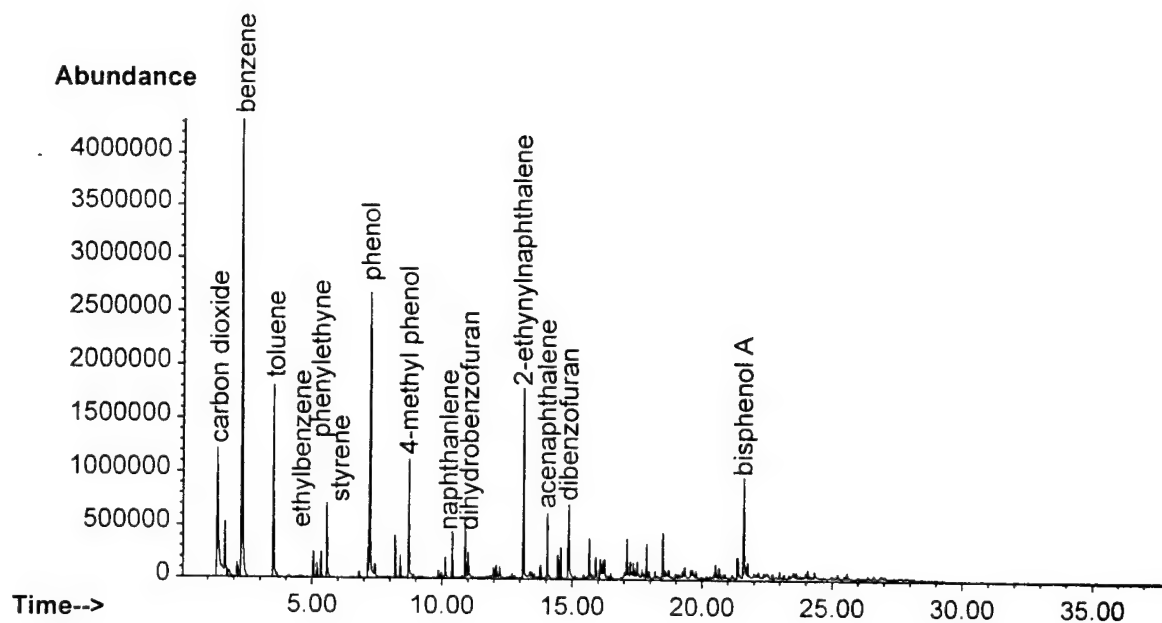




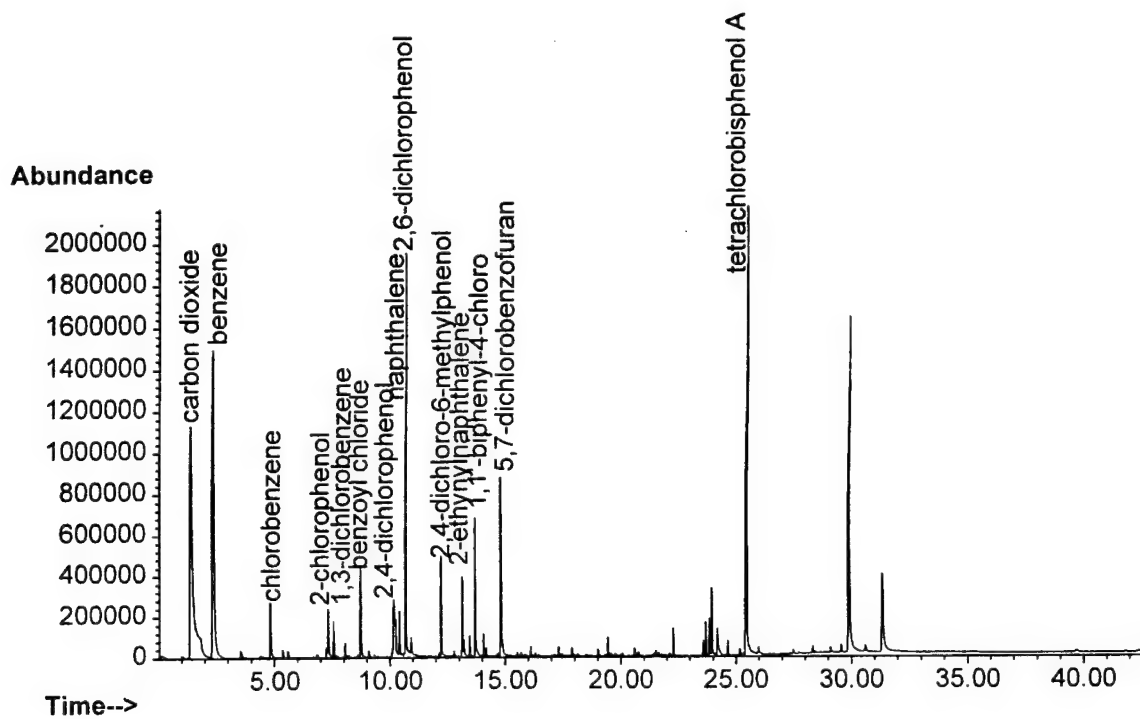
**Figure C.5** Simultaneous-TGA/DSC results for diphenylester of biphenol C (V).

## APPENDIX D

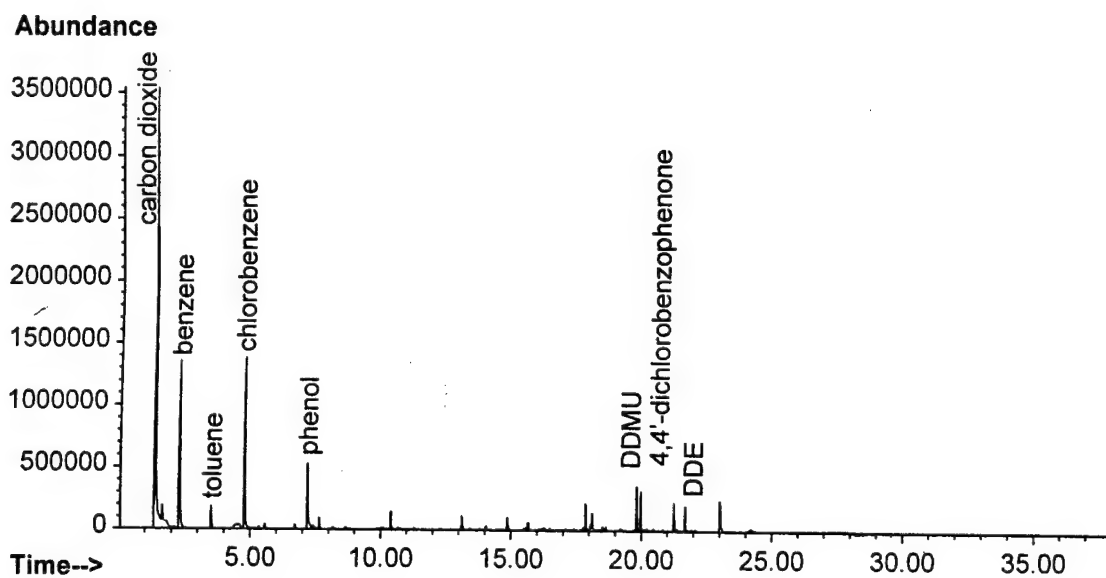
### GC TRACES FROM PYROLYSIS EXPERIMENTS FOR BISPHENOL BASED MATERIALS



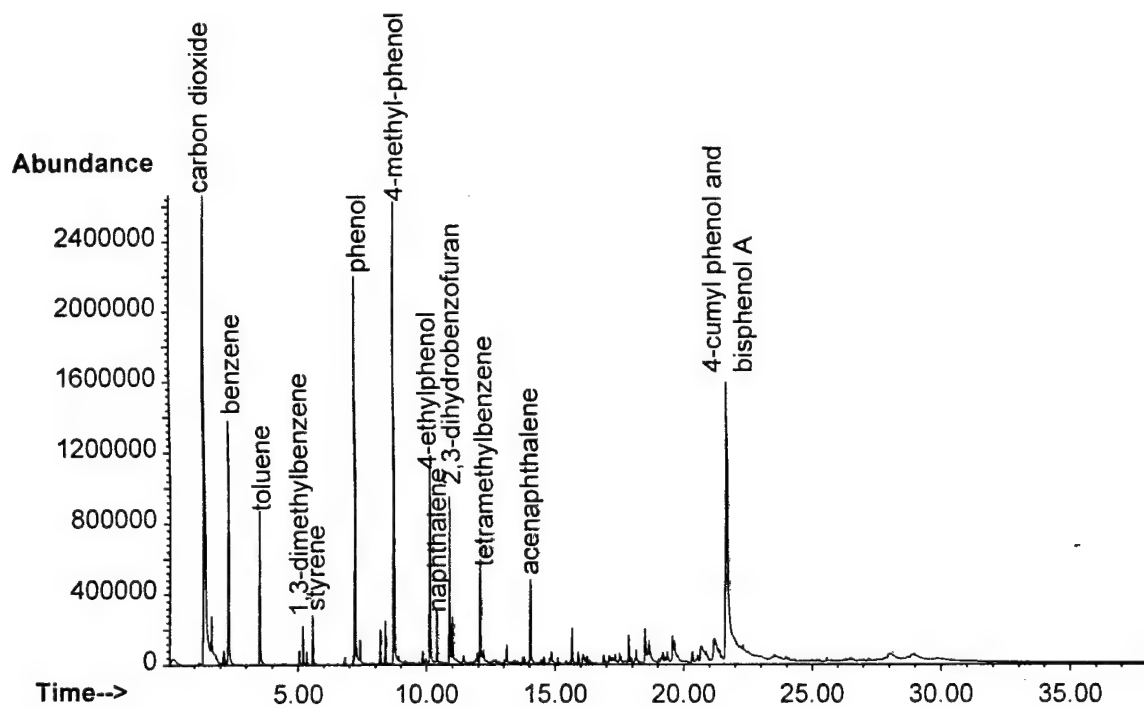
**Figure D.1** GC trace of products from the decomposition of bisphenol A polyarylate (poly-3).



**Figure D.2** GC trace of products from the decomposition of poly-8 (polyarylate from tetrachlorobisphenol A).



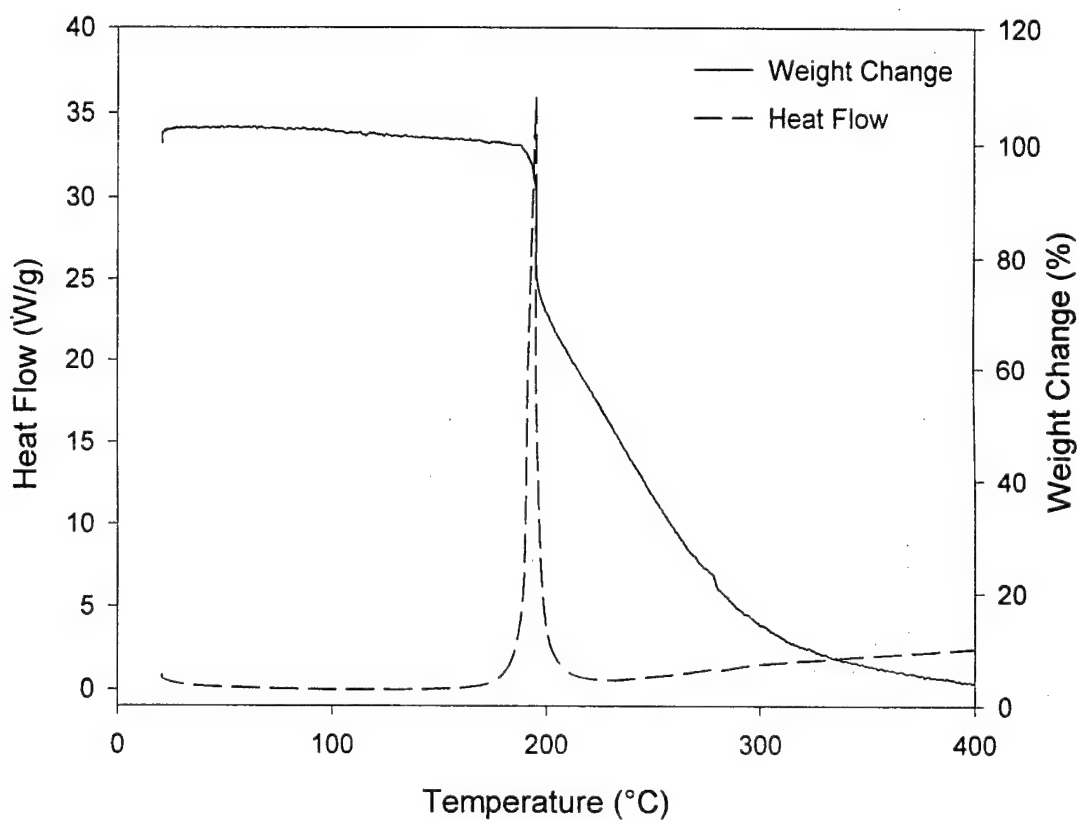
**Figure D.3** GC trace of products from the pyrolysis of poly-1 (bisphenol C polycarbonate).



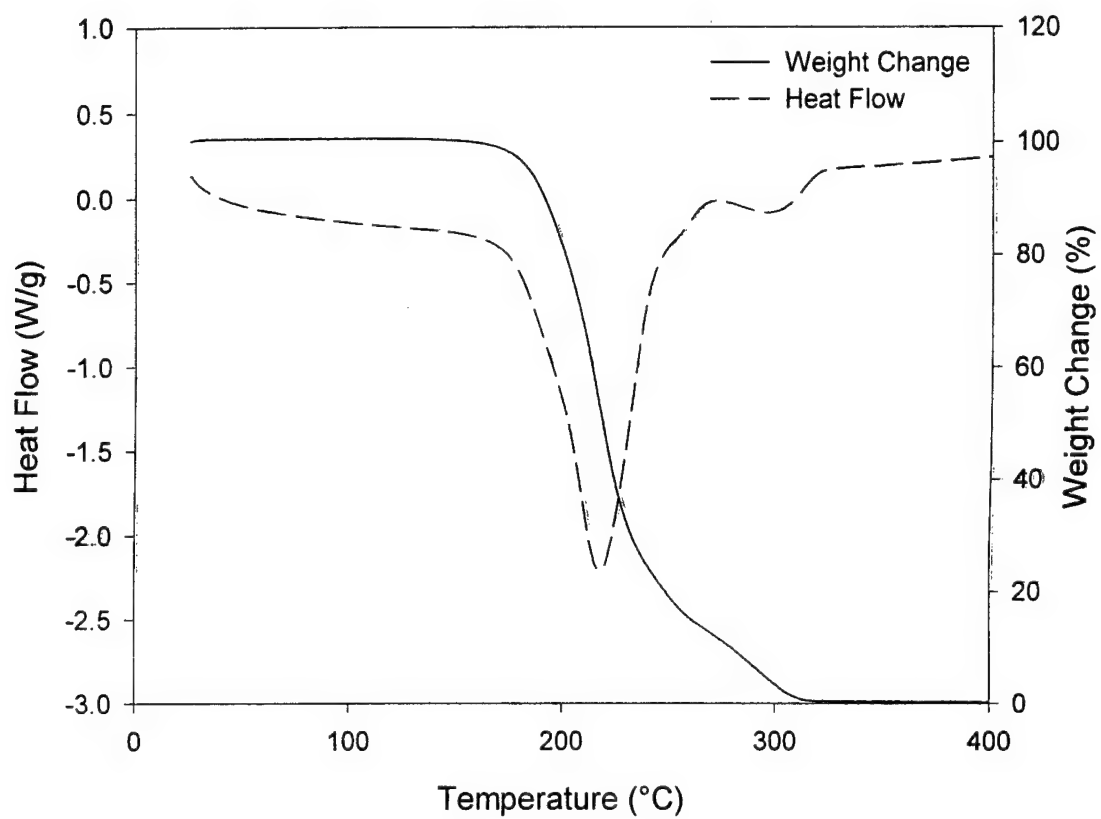
**Figure D.4** GC trace of products from the pyrolysis of bisphenol A polycarbonate.

## APPENDIX E

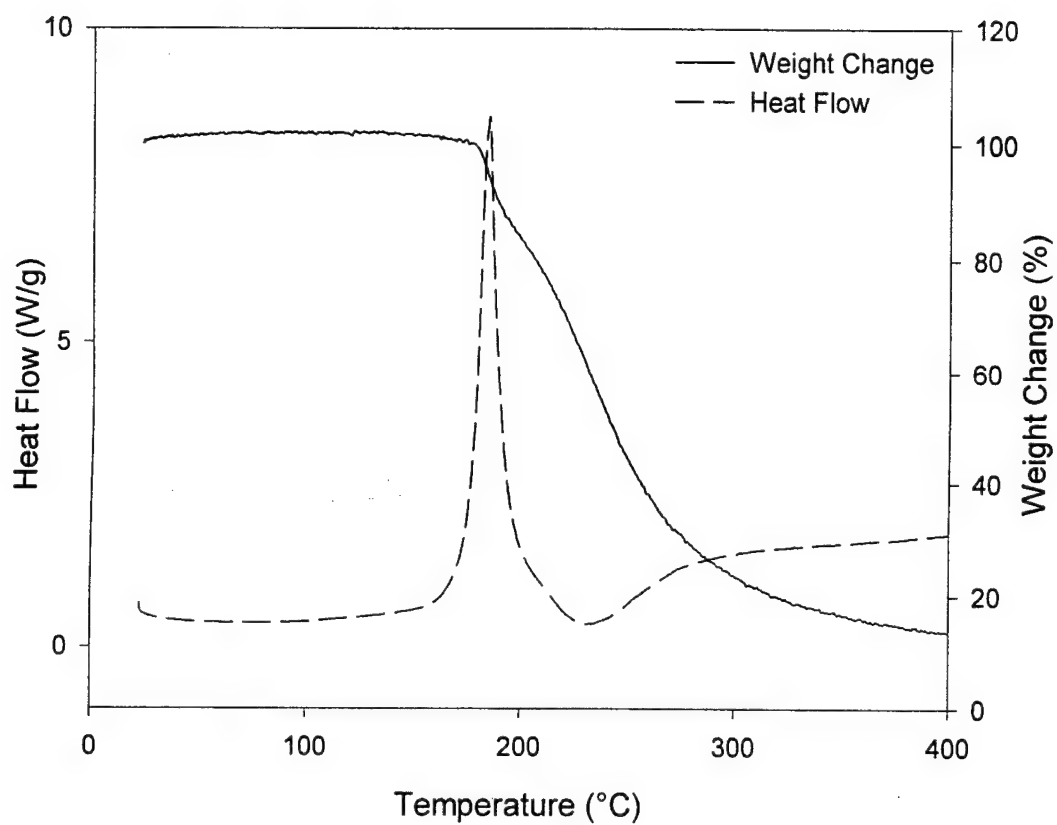
### STA THERMOGRAMS OF POLYCARBODIIMIDES



**Figure E.1** Simultaneous-TGA/DSC thermogram for poly(N-methyl-N'-TEMPO)-carbodiimide (poly-19).



**Figure E.2** Simultaneous-TGA/DSC thermogram for poly(N-methyl-N'-methylbenzyl)-carbodiimide, (poly-20).



**Figure E.3** Simultaneous-TGA/DSC thermogram for co-polycarbodiimide (poly-21).



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